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REACTIONS OF ZIRCONIUM WITH GASES AT LOW PRESSURE[1]

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ABSTRACT

Data on the reaction of zirconium with oxygen, nitrogen, carbon monoxide, carbon dioxide, hydrogen, and water vapor in the micron pressure range are presented. The reaction products are studied by means of electron and X-ray diffraction analysis. When zirconium metal powder is exposed to carbon monoxide or carbon dioxide in the temperature range of 600° to 800°C., both zirconium dioxide and zirconium carbide are formed. In agreement with the work of de Boer and Fast, it is found that ductile zirconium strip can dissolve as much as 38 atom per cent of oxygen without the formation of a new phase.

A new apparatus for the study of gas-metal reactions at low pressure is described.

INTRODUCTION

The early work of J. H. de Boer and his colleagues (1, 2) showed that zirconium has unique properties, in its capacity to sorb gas, which offer special advantages in the production and maintenance of a vacuum in electron tubes. Later work (3, 4, 5) has confirmed that zirconium will react with all the commonly occurring gases at very low pressures. The published data, however, are not in agreement as to the optimum temperature ranges for the sorption of gases by zirconium and, in some cases, information on the chemistry of the gettering process is incomplete. In view of the availability of zirconium metal in purer grades and the promising results obtained in early tests of this material as a getter in certain electron tubes, it seemed desirable to study the metal-gas reactions involved under conditions closely approximating those in actual tubes.

The gases included in the present study were oxygen, nitrogen, carbon dioxide, carbon monoxide, hydrogen, and water vapor. After a high temperature outgassing of the zirconium in vacuum, sorption measurements were made at approximately 25°C., 400°C., and 800°C. Studies were made to determine the rate of cleanup of gas and the minimum and optimum temperatures for the sorption of these gases. Low-pressure gas analysis techniques (6) were employed to follow the course of the reactions occurring. The compounds formed in several cases were identified by electron and X-ray diffraction analysis.

EXPERIMENTAL PROCEDURE

General

In general, the gas sorption measurements were made on coatings of zirconium powder applied to molybdenum anodes of a standard type by

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the spray method. The coating weight was 4 ± 1 mg. per sq. cm. and the coated area approximately 25 cm.[2] The coated anodes were mounted in a 772 Nonex glass bulb of approximately 300 cc. capacity. These bulbs were sealed to a glass apparatus, evacuated and baked in an oven for 1 hour at 450°C. The coated anodes were outgassed by heating to 1300°C. for ten minutes employing the high-frequency induction method. In the gas sorption studies, the high-frequency induction method of heating was used at the higher temperatures and an oven at the lower temperatures. An optical pyrometer was used where possible for temperature measurement and control, but corrections for bulb absorption and spectral emissivity were not made. A thermocouple was used in the lower temperature ranges.

Ductile zirconium strip, 0.005″ in thickness, formed into tubing approximately $\frac{1}{2}$ in. in diameter to facilitate heating by induction, was mounted in glass bulbs and treated in a similar manner.

Intermittent gas admission method

Two methods have been employed for following the course of the gas-metal reactions. In the first method, the apparatus used was of similar design to that shown in Fig. 1, except that the large volume, V, was omitted and a mercury cutoff was substituted for the capillary flowmeter. The gas to be studied was introduced through a porous lavite plug into a previously calibrated volume and the pressure measured with a McLeod gauge. This known amount of gas was then admitted to the zirconium-coated surface and the decrease in pressure measured as a function of time. Successive doses of gas are thus introduced until the pressure fails to fall to a value of 2×10^{-4} mm. or less in an arbitrarily chosen time of 10 min. Data obtained by this method are shown in Table II.

Capillary leak method

In the second method, the apparatus for which is shown in Fig. 1, a calibrated capillary flowmeter is used to introduce gas continuously at a very slow rate into the chamber containing the zirconium. As shown in the schematic diagram, pure gas is admitted to the evacuated system by raising the gas bottle, H, until the two lavite plugs, G, come in contact with each other. The gas slowly diffuses through the lavite plugs, through the liquid nitrogen trap, T_2, and into the large volume, V (5688 cc.). The gas is admitted from V to the previously outgassed zirconium, E, at a desired rate by means of the capillaries. By opening stopcock, S_5, to the low vacuum, the mercury may be lowered so that the gas will flow from V through capillary C_1, or capillaries C_1+C_2, or capillaries $C_1+C_2+C_3$. Each capillary is approximately 13 cm. long and 0.06 cm. in diameter. The pressures involved are measured with a McLeod gauge, M_1.

The capillary C_1 is calibrated by admitting pure dry gas to V until the pressure is about 0.1 mm. The mercury level in the capillaries is then lowered so that the gas leaks from V through C_1 to the vacuum pump and the pressure drop in V is measured as a function of time. This procedure is repeated for C_1+C_2 and $C_1+C_2+C_3$. Fig. 2 shows this calibration for oxygen.

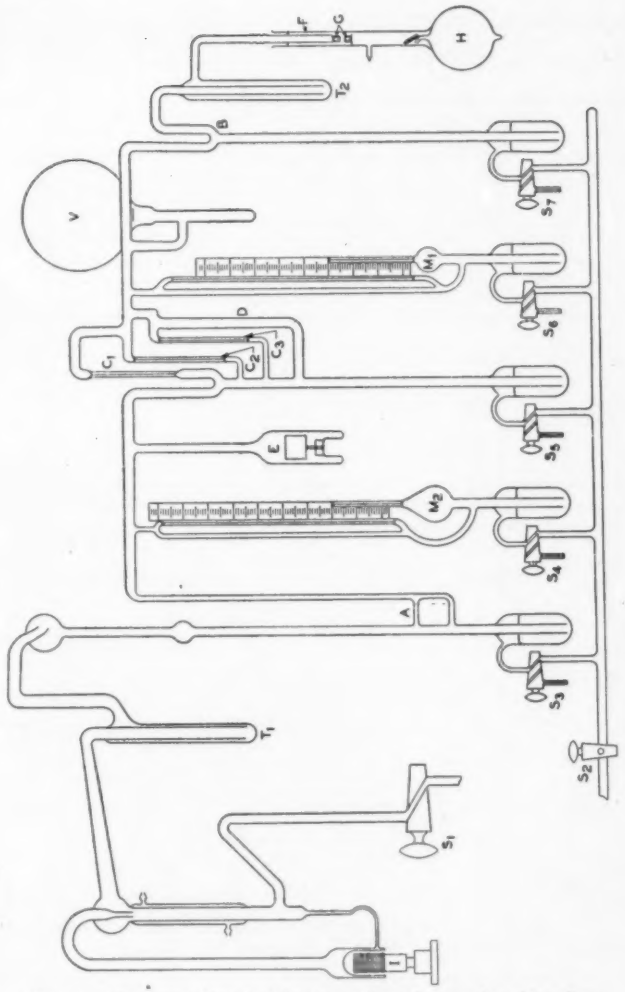

FIG. 1. Apparatus for studying sorption of gases by zirconium

A, B	Mercury cutoffs	E	Sample	H	Gas bottle	S_1–S_7	Stopcocks
C_1–C_3	Capillaries	F	Mercury	I	Heater	T_1, T_2	Traps
D	Bypass	G	Lavite plug	M_1, M_2	McLeod Gauges	V	Large volume

The rate of flow, Q, of a perfect gas from volume V at pressure p_1 is experimentally determined from

$$Q = -\frac{d(p_1 V)}{dt} = -V\frac{dp_1}{dt} \qquad (1)$$

where Q is in cc. mm./min., when p_1 is expressed in mm. and V in cc. For pure diffusive flow (7) $\frac{dp_1}{dt}$ is a simple function of p_1 when p_2, the pressure on the pump side, is much less than p_1, i.e.,

$$-V\frac{dp_1}{dt} = \gamma p_1 \tag{2}$$

TABLE I. *Analytical data on zirconium powder*

Elements	Per cent by weight	
	Zirconium	Zirconium hydride
Aluminum	<0.01	0.03
Iron	<0.01	0.04
Calcium	0.43	0.60
Magnesium	<0.005	0.15
Silicon	0.03	0.05
Oxygen*	3.2	1.8
Sulphur	0.01	0.02
Hydrogen	0.09	1.9

* Oxygen contents were computed from values obtained from gain in weight on ignition and were not corrected for impurity content.

TABLE II. *Sorption of gases by powdered zirconium*
Intermittent method

Gas	25°C.		100°C.		200°C.		400°C.		800°C.	
	cc. mm.	cc. mm./ mg.	cc. mm.	cc. mm./ mg.	cc. mm.	cc. mm./ mg.	cc. mm.	cc. mm./ mg.	cc. mm.	cc. mm./ mg.
Oxygen	40	0.50	42	0.53	45	0.52	60	0.75	1300	16.3
Hydrogen	16	0.20	654	8.17	654	8.17	*	—	†	—
Nitrogen	0	—	0.8	0.01	1	0.01	21	0.26	425	5.3
Carbon monoxide	2	0.03	6	0.08	12	0.15	61	0.75	1000	12.5
Carbon dioxide	1	0.01	2	0.03	8	0.10	47	0.59	850	10.6

* Partial dissociation.
† Complete dissociation.

where γ is the pumping admittance of the capillary and is a function of the temperature and molecular weight of the gas. Integrating,

$$\log_{10} p_1 = \log_{10} p_0 - \frac{\gamma}{2.3V}(t - t_0) \tag{3}$$

where the subscript zero designates initial values of p_1 and t. Thus the admittance γ of the capillary is determined from the slope of the straight line obtained from a plot of $\log_{10} p_1$ against t. For example, as shown in Fig. 2, the negative slope $\gamma/2.3V$ for C_1 is 7.47×10^{-4} min.$^{-1}$ and the admittance γ is 9.78 cc./min. Then Q (rate of flow for oxygen) $= \gamma \cdot p$ (cc. mm./min.) and can be calculated for different values of p_1. When ideal

gases other than oxygen are used, γ is found to vary inversely with the square root of the molecular weight. Thus

$$\frac{\gamma_2}{\gamma_1} = \frac{\sqrt{M_1}}{\sqrt{M_2}}$$

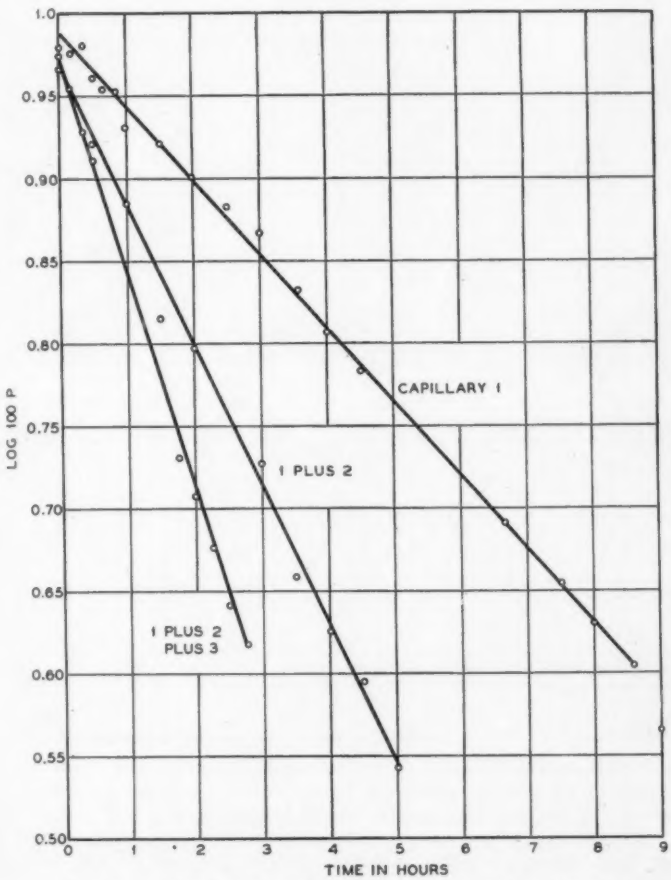

FIG. 2. Calibration of capillaries for capillary leak method

Also, the admittance of a capillary can be calculated when its diameter and length are accurately known (7).

In making a test run on the sorption of gas by the zirconium, the pressure in V is recorded and then the gas is allowed to pass through a given capillary or capillaries to the zirconium. The pressure in V is recorded after

1, ½ or ⅓ hr. when capillary C_1, C_1+C_2, or $C_1+C_2+C_3$ are used respectively. The pressure in V is raised again to approximately the initial pressure and the procedure repeated. The total cc. mm. of gas passing through the capillary is calculated from the sum of the $\bar{Q}\ t$ (Min)

$$\bar{Q}_0 t_0 + \bar{Q}_1 t_1 \cdots + \bar{Q}_x t_x$$

Also the rate of flow can be varied by changing the initial pressure, p_0. Data obtained by this method are shown in Table III.

TABLE III. *Sorption of gases by powdered zirconium*

Capillary leak method

Material	Designation	Gas	Temp.	Q	Gas Sorbed	Gas Sorbed
			°C.	*cc. mm./min.*	*cc. mm.**	*cc. mm./mg.*
Powdered zirconium	#23	Oxygen	25	1.0	35	0.38
			400	1.0	181†	1.99
Molybdenum anode	#18	Oxygen	25	1.0	1.3	—
			400	1.0	1.2†	—
Powdered zirconium	#41	Nitrogen	500	1.0	79	0.71
	#43	Nitrogen	500	1.0	118	1.00
	#52	Nitrogen	800	1.0	180	1.46
Powdered zirconium	#46	Carbon monoxide	25	1.0	0.0	0.0
			500	1.0	60.7	0.43
	#47	Carbon monoxide	800	1.0	548	3.65
Powdered zirconium	#54	Carbon dioxide	25	1.0	0.0	0.0
			500	1.0	73	0.57
			800	1.0	389†	3.04
Powdered zirconium	#49	Hydrogen	25	1.0	11.6	0.09
			350	1.0	1706†	13.33

* Values reported indicate the amounts of gas sorbed before the residual pressure over the zirconium exceeds 1×10^{-2} mm., with the gas flowing at the specified rate.

† These values do not include the gas sorbed at the lower temperature.

Zirconium

The zirconium metal powder and the ductile zirconium sheet used in these experiments were obtained from Foote Mineral Company; the zirconium hydride was supplied by Metal Hydrides, Inc. These materials contained as impurities calcium, magnesium, silicon, iron, aluminum, carbon, and oxygen. Table I shows typical analyses of the powdered materials.

The particle size range of the zirconium powder studied was 1 to 8 microns, with occasional particles as large as 15 microns. The specific surface area of one sample as measured by adsorption of gas at low temperature (8) was 8.3 cm.²/mg., which is equivalent to the surface area of smooth spheres, 1.1 microns, in diameter. Thus the surface area immediately available to gas adsorption was greater than would be expected

from 5 micron particles. This is due to the irregular shape of the particles as revealed by microscopic examination. The zirconium hydride powder had a particle size range of 1 to 2 microns. Fig. 3 shows electron micrographs of zirconium in comparison with zirconium hydride powder.

X-ray diffraction analysis of the powdered material did not reveal any evidence of oxide or nitride. Only the zirconium structure was found.

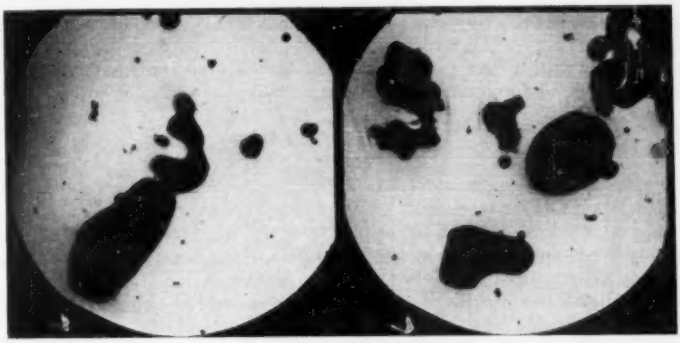

FIG. 3a. Electron micrograph of zirconium powder. 2700×

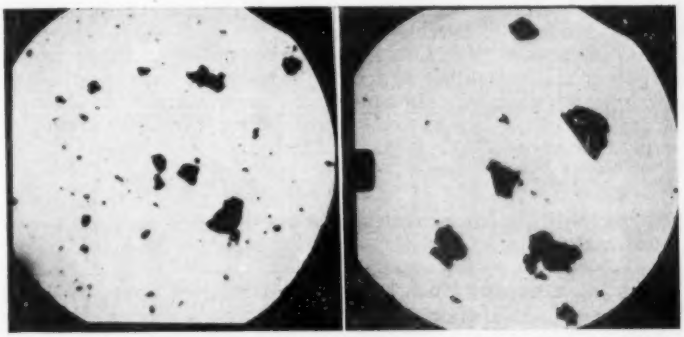

FIG. 3b. Electron micrograph of zirconium hydride powder. 2700×

Binder

In early applications as a getter in electron tubes, nitrocellulose dissolved in amyl acetate was used as a temporary binder for the powder. For high-voltage tubes a permanent binder was needed, and colloidal silicic acid, prepared by the hydrolysis of ethyl silicate, was proposed for this purpose (10). It had the further advantage of not giving gaseous products during outgassing and operation. Colloidal silicic acid was, therefore, used as a binder in these studies. The amount of binder usually used was 2 to 5 per cent. In comparison with coatings applied with the nitrocellulose binder, the addition of silica up to 5 per cent did not appear to affect

the efficiency of the getter. Also, no difference in behavior was observed when zirconium containing no binder was heated in a platinum crucible.

Gases evolved on heating in vacuum

The gas evolved when a zirconium-coated molybdenum anode is heated in vacuum at 1300°C. is mainly hydrogen with a small amount of carbon monoxide. In one typical case, for example, an analysis of the gas showed it to be 99.1 per cent by volume of hydrogen and 0.9 per cent by volume of carbon monoxide. The hydrogen is probably introduced into the metal as a result of washing the powder with hydrochloric acid, a treatment employed to reduce the impurity content.

EXPERIMENTAL DATA

Oxygen

After outgassing the zirconium at a temperature of 1000°C. or greater, zirconium powder will take up approximately one atom per cent of oxygen at room temperature. Upon the basis of surface area measurements, this is equivalent to approximately two atom layers.

Fig. 4 shows the results of an experiment in which the gas is allowed to flow intermittently into the reaction chamber. After 430 cc. mm. of oxygen had been sorbed (4.30 cc. mm./mg. Zr), the residual gas over the zirconium amounted to 0.75 cc. mm. and was found on analysis to be oxygen 90%, nitrogen 4.0%, hydrogen 3.1%, carbon dioxide 2.0%, and carbon monoxide 0.9% by volume.

X-ray diffraction analysis of zirconium powder coatings which had sorbed 10 or more atom per cent of oxygen showed the presence of monoclinic zirconium dioxide. The much purer ductile zirconium sheet did not show any evidence of the zirconium dioxide structure after taking up 38.3 atom per cent oxygen.

Nitrogen

The reaction of nitrogen with zirconium does not occur at room temperature and occurs at 400°C. only very slowly. At 800°C., however, this gas is cleaned up very rapidly.

On heating a sample which had sorbed a total of 13 atom per cent to 1300°C., no gas was liberated; this indicated that a very stable compound had been formed. X-ray diffraction patterns obtained on a sample thus exposed to nitrogen showed evidence of compound formation, the compound being identified as zirconium nitride.

Since it is common practice in manufacturing operations to seal-in tubes containing zirconium-coated plates while flushing with a stream of purified nitrogen, it was of interest to determine whether sufficient nitrogen was gettered during the seal-in operation to impair the gettering efficiency of the coated anode. In order to determine whether exposure to nitrogen decreases the ability of zirconium coatings to absorb oxygen, a zirconium-coated anode was sealed-in in an atmosphere of nitrogen, and then subjected to the usual outgassing and exposure to oxygen at 400°C. as described in the preceding section. The temperature of the plate during the seal-in was estimated to be 400° to 500°C. In this case, the behavior

of the coating with respect to efficiency of cleanup of oxygen was normal. It was, therefore, concluded that ordinary seal-in operations, using nitrogen as the inert atmosphere, do not seriously impair the gettering efficiency.

Carbon dioxide

Using the same methods outlined above, carbon dioxide was studied. The amount sorbed in one case at 400°C. was 0.45 cc. mm./mg. zirconium. At 800°C. the rate of uptake was rapid. In one case working in the pressure range of 10^{-1} to 10^{-3} mm., 28.5 cc. mm./mg. zirconium were sorbed

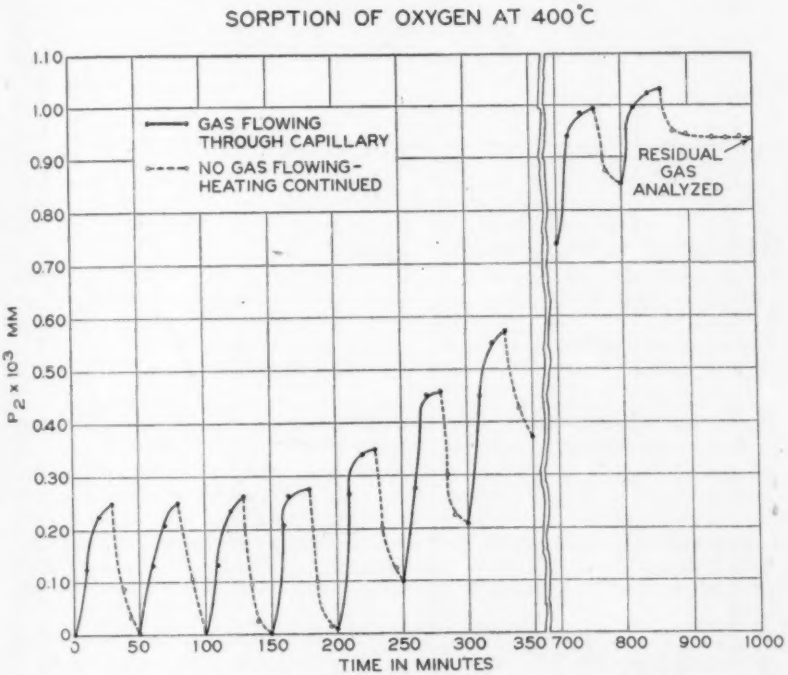

FIG. 4. Sorption of oxygen at 400°C. by zirconium powder on molybdenum

without reaching saturation although the rate of reaction had decreased greatly. When this sample was heated to 1300°C. in vacuum, no gas was given off. When it was analyzed by diffraction methods, evidence was obtained indicating the presence of zirconium oxide, ZrO_2, and zirconium carbide, ZrC. It is clear, then, from both chemical and X-ray evidence that stable chemical compounds are formed when carbon dioxide is cleaned up by zirconium at a temperature of approximately 800°C. The structures of zirconium nitride and zirconium carbide are isomorphous and their cell constants are nearly equal. Also, the scattering powers of nitrogen and carbon are nearly equal. One must therefore depend entirely on the

history of the sample for positive differentiation between the two compounds.

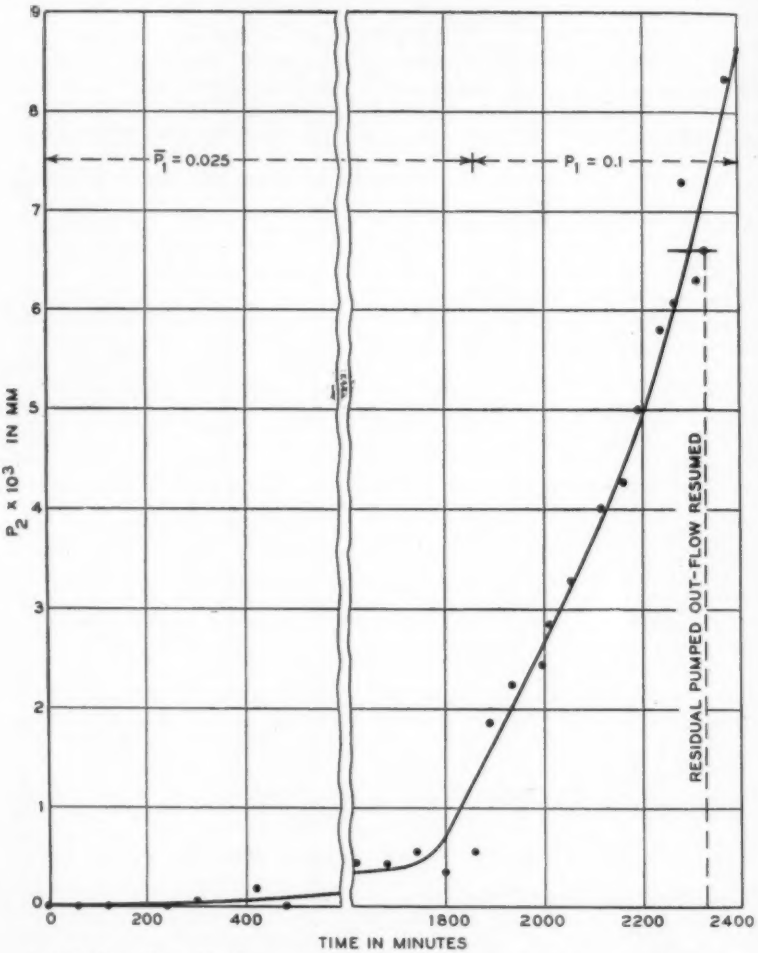

FIG. 5. Sorption of hydrogen at 300°C. by zirconium powder on molybdenum

Carbon monoxide

The behavior of carbon monoxide with respect to zirconium was very similar to that of carbon dioxide. Both chemical and X-ray evidence supports the conclusion that zirconium dioxide and zirconium carbide are

formed. On samples exposed either to carbon dioxide or to carbon monoxide it was found, by X-ray and electron diffraction analysis, that zirconium dioxide was distributed throughout the material and zirconium carbide was present on the surface.

Hydrogen

Hydrogen is unique among the gases studied in that the reaction with zirconium is reversible, the gas being completely liberated at approximately 800°C. The optimum temperature for cleanup of hydrogen was found to be 300°C. A typical curve obtained by the capillary leak method for the sorption of hydrogen by zirconium at 300°C. is shown in Fig. 5. The total amount of gas sorbed was in excess of 17 cc. mm. hydrogen/mg. zirconium.

Water vapor

In the range of 200° to 350°C., water vapor is cleaned up at about the same rate as oxygen. On raising the temperature of the specimen thus treated, hydrogen is liberated. On exposing a zirconium-coated metal plate to water vapor in the temperature range of 700° to 800°C., hydrogen is formed and liberated in the system. Thus, in order to clean up water vapor efficiently, the temperature of the getter should be maintained within the range of 200° to 350°C. unless an auxiliary getter is at a suitable location elsewhere in the tube.

Other metals as bases

Zirconium metal powder applied by the spray or paint method to other metal surfaces, including iron, nickel and copper, has been tested with good results. It was found, however, that in order to obtain efficient gettering action, the coated surface must be heated to at least 700°C. for a few minutes in order chemically to activate the surface. In addition to the dissociation of the zirconium hydride, this activation probably consists of solution of the protective oxide film which is always present on zirconium after exposure to air. This oxide film is cleaned up by diffusion of the oxide into the metal, thus leaving an active surface for gas reaction.

DISCUSSION

In agreement with the finding of de Boer and Fast (9), we found that ductile zirconium is capable of dissolving more than 38 atom per cent of oxygen in true solid solution. Working with zirconium powder, however, we found that a new phase, monoclinic zirconium dioxide, appears before 10 atom per cent of oxygen has been sorbed, and that a new phase, attributed to zirconium nitride, appears before 15 atom per cent of nitrogen has been taken up. The presence of a considerable concentration of oxygen in the powdered material as it is received for test does not appear to account for the appearance of a new phase since insufficient oxygen had been added to exceed the solubility limit as found by de Boer and Fast (9).

The discrepancies in the literature as to the optimum temperature and the capacity for the sorption of various gases by zirconium are believed to be the result of differences in the purity of the materials studied, and to the

failure in some cases to clean up the surface by heat treating at a temperature sufficient to cause oxygen and nitrogen on the surface to diffuse into the metal. In agreement with Hall, Martin, and Rees (5), it has been found that the sorption characteristics, both as to rate of reaction and capacity, are affected by the purity of the zirconium used.

In view of the results cited in the sections on carbon dioxide and carbon monoxide, it appears that oxygen will diffuse through zirconium much more rapidly than carbon since only carbide was found on the surface by electron diffraction while the oxide was revealed in the bulk material by X-ray diffraction analysis. It should be kept in mind, however, that the oxygen content of the powder initially was high compared to its carbon content.

SUMMARY

A brief summary of gas sorption by zirconium is given in Tables II and III. The optimum temperature for the use of this getter and the amount of gas that can be sorbed at a given temperature range at pressures of less than 1 micron are indicated.

The advantages of zirconium are as follows:

1. Relatively large amounts of gas may be sorbed by zirconium at elevated temperature to pressures of less than 10^{-5} mm. X-ray and electron diffraction analysis indicates that the gases can diffuse into the metal, thus leaving a pure metal surface for reaction with additional gas.
2. Zirconium powder applied to a molybdenum anode with a silica binder and preheated at 1300°C. in vacuum can be operated at a temperature of 800°C. in vacuum without evolution of gas.
3. With the exception of hydrogen, zirconium forms very stable solid solutions or compounds with the gases studied.
4. The presence of mercury vapor does not interfere with the sorption of gases by zirconium as is the case in barium, magnesium, and barium-magnesium alloy type getters.

The chief disadvantage of zirconium as a getter is that the optimum temperature for the sorption of hydrogen is too low for the effective cleanup of such gases as nitrogen and the oxides of carbon. If the zirconium-coated part is to operate at a temperature much in excess of 300°C., a supplementary getter of the barium or barium-magnesium type should then be included to take care of the hydrogen.

ACKNOWLEDGMENTS

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Any discussion of this paper will appear in the discussion section of Volume 93 of the Transactions of this Society.

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THE QUANTITATIVE EVALUATION OF OXYGEN IN ZIRCONIUM[1]

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ABSTRACT

Two methods for the determination of oxygen are reviewed and applied to the analysis of zirconium. The first is indirect and involves combustion of the metal and calculation of the oxygen content by difference. Corrections must be made for hafnium and other oxygen absorbing, inert, or volatile contaminants and the method is, therefore, useful only for control purposes or where relatively large amounts of oxygen are present.

The second procedure is a direct determination of the zirconium oxide content by vaporization of the metal in chlorine gas. The residue must be corrected for side reactions with carbon. The approximate precision and accuracy of the method have been evaluated by the analysis of zirconium with known oxygen content. The precision is approximately 0.02 per cent with 2.0 g. samples and there are indications that results are a little low.

Analysis of available zirconium shows the following approximate oxygen values: Foote Mineral (wire), 0.04 per cent; Bureau of Mines (melted), 0.08 per cent; and Westinghouse (powder), 0.13 per cent.

The micro-structures of heat treated zirconium wires with and without added oxygen are shown. They indicate why, in some cases, hardness increased with heating alone. Microhardness measurements on a series of oxygen-doped wires have provided a correlation between oxygen content and hardness. The hardness of zirconium increases roughly 50 V.P.N. for each 0.1 per cent of added oxygen and metal containing more than about 0.2 per cent oxygen is probably not cold workable.

INTRODUCTION

The malleability of zirconium depends primarily on the control of oxygen and nitrogen in the metal. These gases form solid solutions and in relatively small amounts result in increased hardness and loss of workability. It is an academic question whether oxygen dissolves as such, or first forms zirconium oxide which in turn dissolves in the metal.

As it is practically impossible to produce zirconium, at least commercially, without the introduction of small amounts of these gases, the relationship between the oxygen and nitrogen content of the metal and hardness and workability is of considerable practical importance.

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Knowledge of the permissible limits of oxygen is also of value in determining the feasibility of a certain line of approach to zirconium production. Thus in the reaction $ZrO_2 + 2Ca = Zr + 2CaO$, thermodynamic calculations indicate that a double reduction with calcium using 50 per cent excess for the first reduction and 30 per cent excess for the second should yield a product containing approximately 0.02 per cent ZrO_2 or 0.005 per cent O. In practice this has not been realized, the oxygen content of such metal being approximately 0.10 per cent.

The object of this paper is to present certain methods which have been used to evaluate the oxygen content of zirconium as produced by three different processes. The work was undertaken with the expectation that the basic techniques developed could be applied to other rare metals. The approximate accuracy of the methods was estimated by the analysis of zirconium wires to which known amounts of oxygen had been added.

Photomicrographs of zirconium are included which shed some light on the micro-hardness values obtained on wires with and without added oxygen. The discussion will be limited to those methods of determining oxygen in zirconium which have been applied in the Westinghouse laboratory. These are, first, the determination of the zirconium content by weight gained by combustion, and calculation of the oxide content by difference, and, second, volatilization of zirconium metal in purified chlorine gas at elevated temperatures and determination of the zirconium oxide in the residue.

DETERMINATION OF OXYGEN BY COMBUSTION

This indirect method is of interest because it involves a determination of the hafnium content of the metal. It is applicable to zirconium millings, or powder, and comprises combustion of the metal in oxygen in a platinum boat at approximately 1000°C. The gases are passed through water prior to entering the tube furnace and the tube initially is swept out with argon gas to avoid rapid combustion, especially if the material is in powder form. The argon flow is gradually reduced and the samples finally ignited in pure oxygen. The increase in weight of the sample and a preliminary determination of the hafnium content of the metal permit a fair approximation of the oxygen content.

The hafnium in the metal may be calculated from a determination of the density of its oxide by the pycnometer method (1), using the densities of pure zirconium oxide (5.73) and hafnium oxide (9.74) as given by Von Hevesy, (2) and the formula

$$Xw = \frac{d - 5.73}{0.0401} \times \frac{9.74}{d}$$

where d = density of mixed oxides
Xw = weight per cent HfO_2.

The application of the combustion method presupposes also a more or less complete chemical analysis of the metal for other constituent metals such as Fe or Ca which take up oxygen and yield a high value for oxygen absorption and, therefore, must be corrected for. On the other hand, volatile constituents and those which form volatile oxides, such as molybdenum

and carbon, as well as inert materials, will decrease the value obtained. As an example of the application of this method, a zirconium powder which analyzed CaO 0.1%, Fe 0.05%, Si 0.09%, N 0.06%, Mo 0.07%, and Hf 3.82% was combusted and corrections made for Ca, Fe, Mo, and Hf. The final calculation showed 99.8% Zr plus Hf and 0.2% ZrO_2 plus HfO_2. On the assumption that the oxide was primarily ZrO_2, the oxygen content was approximately 0.05 per cent.

The direct method of analysis to be described showed the oxygen content to be approximately 0.1 per cent. These values are interesting in that they tend to confirm the value found for hafnium content of the oxide used as a starting material. This oxide was prepared by ignition of an oxychloride crystallized from $ZrCl_4$ (Foote Mineral); the hafnium content of zirconium oxides in general use may be appreciably above this figure.

DETERMINATION OF OXYGEN BY VOLATILIZATION OF THE METAL IN CHLORINE

A method which appeared to have merit is the direct determination of zirconium at elevated temperatures in an atmosphere of purified chlorine gas. This procedure is preferable to the former in that a complete chemical analysis is not required; the zirconium oxide which remains as a residue may be separated from most interfering elements by a rather simple chemical analysis and weighed as ZrO_2, from which the oxygen content of the metal may be calculated.

The method as developed at Westinghouse consists essentially in volatilizing the metal as the chloride at 800°C. in an evacuated glass system in a stream of chlorine gas which has been purified by a sulfuric acid scrubber and fractional distillation. The main reaction is $Zr + 2Cl_2 = ZrCl_4$. The chloride which has an appreciable vapor pressure is volatilized and condenses in chambers at either end of the apparatus and the oxygen combined as ZrO_2 remains as a residue in a silica boat. Corrections must be made for side reactions which will be discussed below.

Preliminary investigations were conducted on wires produced by thermal decomposition of the iodide (Foote Mineral) containing known additions of oxygen. The nitrogen content was determined and found to be approximately 0.01 per cent. Experiments were conducted with an ambient furnace temperature of 800°C. and the residues analyzed for ZrO_2 content. The results were low indicating that some oxygen was lost either by volatilization of an oxychloride, or that a reduction of zirconium oxide had occurred with subsequent formation and volatilization of zirconium as $ZrCl_4$. It was noted in these preliminary experiments that samples containing little or no added oxygen yielded black residue indicating the presence of carbon while with samples containing 0.1 per cent or more oxygen the residue was white, indicating that the carbon in these cases had reacted. The presence or absence of carbon in these samples was confirmed by combustion of the residues in oxygen and absorption of the CO_2 in barium hydroxide solution. The presence of carbon was later confirmed by quantitative analysis of several lots of 0.050″ (1.27 mm.) (Foote Mineral) wires and carbon was found to vary in separate lots between 0.01–0.05 per cent. It is known that zirconium tetrachloride may be formed by the reaction between zirconium oxide, carbon and chlorine, and that the rate of reaction is increased at a given temperature if zirconium carbide is

substituted for carbon. The reactions occurring may be expressed as follows:

$$ZrO_2 + 2C + 2Cl_2 \rightarrow ZrCl_4 + 2CO \quad (1)$$

$$ZrO_2 + 2ZrC + 6Cl_2 \rightarrow 3ZrCl_4 + 2CO \quad (2)$$

It was, therefore, found necessary to analyze the zirconium prior to volatilization, as well as the final residue for carbon, so that the carbon used up could be known and its equivalent in terms of ZrO_2 or oxygen calculated.

Carbon analyses were made by direct combustion in oxygen at 1200°C. in the case of zirconium wires, and at 1000°C. for residues containing free carbon. The carbon dioxide evolved was passed over heated copper oxide to insure oxidation of CO to CO_2 and the latter gas absorbed in standard barium hydroxide solution. The carbonate formed was determined by titration of the unused barium hydroxide with standard hydrochloric acid using phenolphthalein as an indicator.

The details of operation may be conveniently described by reference to Fig. 1 and the accompanying legend. The operations may be divided into the following steps: a) Collection of liquid chlorine, b) Evacuation and preparation of reaction chamber, c) Distillation of metal as the chloride and removal of residue, and d) Determination of zirconium oxide and correction for side reactions with carbon.

Referring to Fig. 1, tank chlorine (1) gas is admitted from tank through the needle valve (2) into a sulfuric acid bubbler (4) and thence to trap (6). The stopcock (8) is open to the atmosphere as shown until residual air has been swept out. Then the stopcock is closed and a vacuum bottle containing solid CO_2 and a convenient liquid such as cellosolve acetate is brought up on the trap (6) and the passage of chlorine continued until a sufficient quantity of liquid chlorine has been collected. At this point, stopcock (5) is closed and the chlorine in the trap frozen out with liquid air. The vapor pressure of chlorine is less than 0.001 mm. at liquid air temperature. The reaction chamber is made of Pyrex glass with the exception of the central heating chamber which may be either Pyrex, Vycor tubing or quartz with graded seals at the Pyrex bulbs. The chamber and the traps (16 and 17) are first baked out at 500°C. for two to three hours by placing an air oven, not shown in Fig. 1, over the complete unit. During baking, the unit up to stopcock (8) is evacuated through the stopcock (13) and liquid air trap (11). The pressure is read by means of thermocouple gauge (12). The vacuum system comprises a three stage oil diffusion pump with Octoil-S oil and a Welch Duo seal backer pump. The closed manometer (9) is filled with Octoil-S. After thoroughly baking and cooling, stopcock (13) is closed and tank nitrogen admitted to atmospheric pressure through stopcock (15), the pressure being read on the manometer. The reaction chamber is then disconnected at the universal joint (14) and the sample or samples introduced in silica boats into the central heating zone. Stopcock (13) is then opened and the entire apparatus is exhausted up to stopcock (5).

A split tube furnace is brought up as shown in (20) and the temperature raised to 800°C. while pumping continuously. When a vacuum of 1–2 microns has been obtained, stopcock (13) is closed and the liquid air trap removed from chlorine condensing trap (6) and replaced with a CO_2 trap.

The chlorine pressure is read on manometer (9) and, in most cases, is maintained at $\frac{1}{2}$–1 atmosphere during the reaction. The zirconium volatilizes as $ZrCl_4$ and collects as a white sublimate in the bulbs (18 and 19).

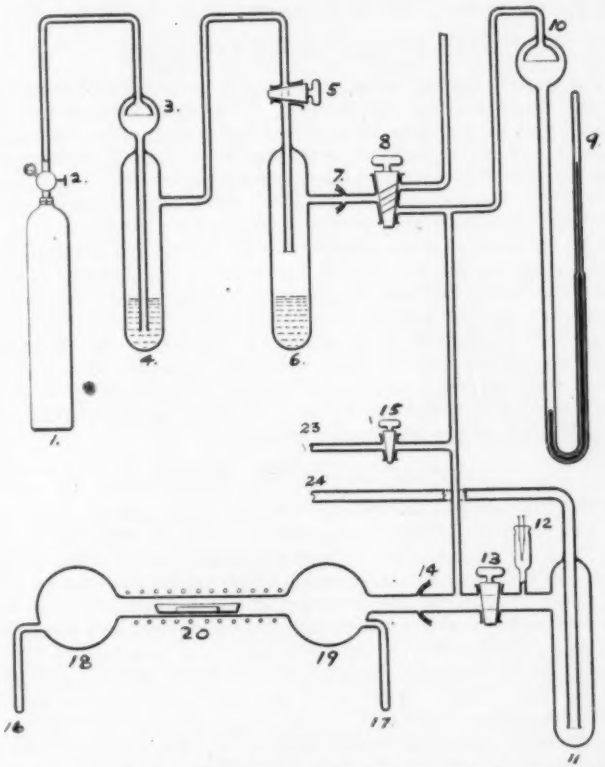

FIG. 1. Apparatus for determination of oxygen in metals. 1. tank chlorine, 2 needle valve, 3. splash trap, 4. sulfuric acid bubbler, 5. one-way stopcock, 6. liquid chlorine trap, 7. universal joint, 8. two-way stopcock, 9. closed manometer Octoil-S, 10. splash trap, 11. liquid air trap, 12. thermocouple gauge, 13. one-way stopcock, 14. universal joint, 15. one-way stopcock, 16–17. chlorine traps, 18–19. condensation bulbs, 20. furnace windings, 21. silica boat, 22. zirconium metal, 23. to nitrogen tank, 24. to diffusion pump and backer pump.

The reaction is exothermic and the metal glows. The absence of incandescence and evolution of chloride is taken as an indication of completion of the reaction.

At this point the tube is allowed to cool to room temperature, stopcock (8) is closed and residual chlorine is frozen out by liquid air traps placed under (16 and 17). Tank nitrogen is then admitted to atmospheric pressure through stopcock (15) the gas being passed through a scrubber con-

taining water and thence through a grounded metal tube before passage into chamber. This is necessary to prevent the formation of a static charge which if allowed to accumulate will result in loss of residue in the boat upon its removal from the tube. The apparatus is then disconnected, the boat removed and the residual carbon determined as previously described.

DETERMINATION OF ZrO_2 IN RESIDUES

After the carbon determination, the residue is transferred to a platinum crucible and fused with sodium bisulfate. The melt is extracted with dil. sulfuric acid and the solution filtered to remove silica. In most cases iron is sufficiently low in the original metal to be completely removed in the volatilization, and the zirconium may be separated with "Cupferron" from 10 per cent by volume sulfuric acid solution, ignited and weighed as ZrO_2 (3). For materials high in iron a preliminary separation of iron as sulfide from an ammoniacal tartrate solution is required prior to the final determination of the zirconium with cupferron. The impurities generally encountered in zirconium are silicon, iron, calcium and magnesium. In case metals are present which would be separated with cupferron other than iron, it is preferable to separate the zirconium as phosphate by established procedures from strongly acid solutions. To the oxide residue found, there must be added an amount equivalent to the difference between carbon in the original metal and residual carbon after volatilization of the chloride, according to the reactions above.

APPLICATIONS OF THE METHOD

The method of analysis described above has been applied to the evaluation of oxygen in zirconium produced by thermal dissociation (Foote Mineral), magnesium reduction of zirconium chloride (Bureau of Mines), and calcium reduction of zirconium oxide (Westinghouse). An attempt has also been made to establish the accuracy of the method by the analysis of Foote Mineral wires to which known amounts of oxygen had been added.

In the latter experiments, samples of 0.050″ (1.27 mm.) diam. wires were cleaned with fine emery paper, bent in hair pin form, and clamped within a stoppered vacuum bottle. The bottle was then exhausted to less than 1 micron, the wires heated to 1400°C. for ½ hr., cooled and weighed. They were then reclamped in the bottle, heated to 1400°C. and a calculated volume of oxygen admitted. Oxygen absorption was rapid, the pressure falling to less than 1 micron in about 1 minute. Heating at 1400°C. was continued for 5 minutes, the wires cooled, removed, and reweighed. The per cent of oxygen was calculated from the difference in weighings. The analytical results are given in Table I for the various samples.

The results obtained on wires doped with known amounts of oxygen as shown in Table I are also plotted in Fig. 2. The difference between the amounts added and the amounts found are believed reasonable for the quantities involved and the character of the determination.

HARDNESS AND STRUCTURE OF ZIRCONIUM WIRES CONTAINING OXYGEN

Coincident with the development of the method of analysis, the microstructure of oxygen-doped zirconium wires was studied. The structure of zirconium is dependent more upon the heat treatment to which the metal

has been subjected than its oxygen content, at least when the oxygen contamination is small. The pictures (Fig. 3–12) are longitudinal sections of heat treated wires, some with added oxygen, and show progressive sections from the cold end into the hot zone. The fields are approximately one-half the thickness of 0.050″ (1.27 mm.) diam. wire. Fig. 3 to 6 are sections of a Foote Mineral wire which was heated to 1400°C. for one hour in vacuo, the ends being held in clamps as already described. Fig. 3 shows the structure near the end which did not get very hot and is, therefore, substantially the appearance of the original wire. (Past history unknown.) Fig. 4 and 5, the fields of which actually adjoin, show a transition region near the end of the clamp where the wire began to get visibly hot. There is a sharp change near the right side of Fig. 5 from a columnar to a martensitic

TABLE I. *Analysis of zirconium for oxygen*

Material	Oxygen present, %	Oxygen found, %	Deviation, %
Foote mineral, 0.050″ (1.27 mm.) wire	0.08	0.10	+0.02
Foote mineral, 0.050″ (1.27 mm.) wire	0.10	0.14	+0.04
Foote mineral, 0.050″ (1.27 mm.) wire	0.34	0.28	−0.06
Foote mineral, 0.050″ (1.27 mm.) wire	0.34	0.31	−0.03
Foote mineral, 0.050″ (1.27 mm.) wire	0.36	0.33	−0.03
Foote mineral, 0.050″ (1.27 mm.) wire	0.50	0.44	−0.06
Bureau of Mines, melted, billet # 26 3″ diam. (76.2 mm.)		0.09	
Bureau of Mines, billet # 26 at 0.100″ (2.54 mm.)		0.06	
Avg		0.08	
Westinghouse Zr powder Ca reduction, oxide		0.14	
Westinghouse Zr powder Ca reduction, oxide		0.12	
Avg		0.13	
Foote mineral, wire 0.050″ (1.27 mm.) as received, Lot A		0.03	
Foote mineral, wire 0.050″, Lot B		0.05	
Avg		0.04	

structure and thereafter a gradual fining until the uniformly hot portion of the wire is reached in Fig. 6. The grain size is large, however, the grain boundary in the center of Fig. 6 crossing the diameter of the wire. Grains in this region were visible 2 to 4 mm. long. A wire to which 0.2 per cent oxygen was added when hot had substantially the same structure up through the transition region (Fig. 7). The martensitic structure in the hot zone is more apparent (Fig. 8) but the grain size is still large.

Similar studies were made of a zirconium wire produced by the Bureau of Mines (Fig. 9–12). There is a transition region as before wherein considerable crystal growth takes place but the columnar structure is absent. The acicular structure in the hot zone is much more pronounced and much finer than in the other wire. The grain size is again very large. All the photographs of the hot portions of the wires may be assumed to be quenched structures since the wire cooled quickly when the current was turned off.

The structure is almost identical with that observed in titanium by Dean and his coworkers (4). The acicular structure will probably revert to a polyhedral if cooled slowly from above the transition point.

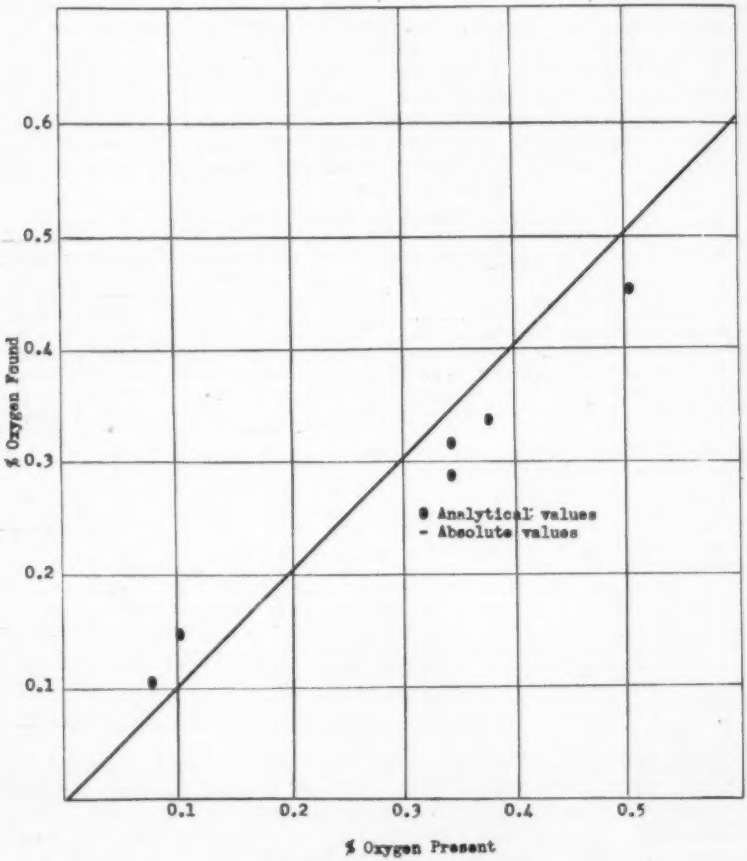

FIG. 2. Accuracy of method

Micro-hardness measurements were taken along the wires and, in some instances, impressions were taken in the fields shown. The values are listed in Table II with reference to the pictures. Foote Mineral wire shows a marked increase in hardness with heating alone. This fact causes speculation whether the dark spots in Fig. 3 may not be oxide inclusions which go into solution upon heating, thereby hardening the metal. Yet the hardness has not increased in Fig. 4 where the inclusions have disappeared, nor even

FIG. 3 FIG. 4

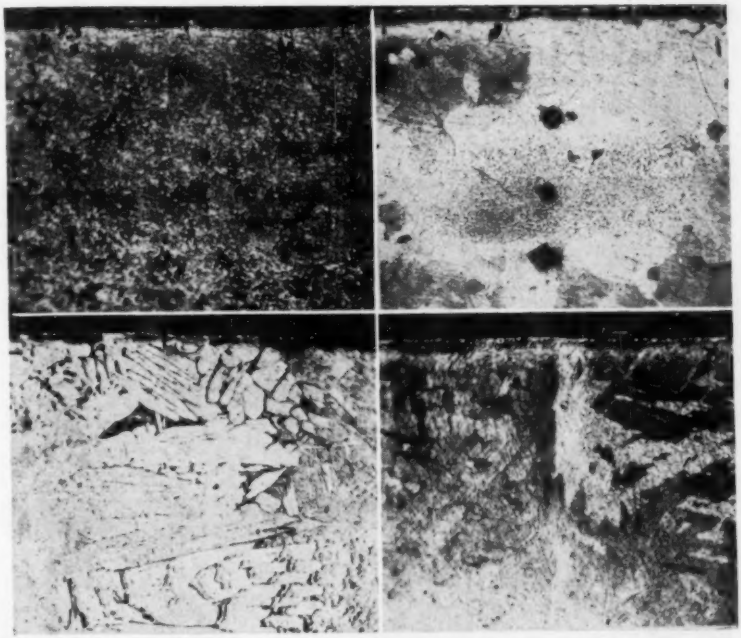

FIG. 5 FIG. 6

FIG. 3–6. Foote Mineral Zr, heat treated in vacuo 1 hr. at 1400°C.; progressive sections from cold end to hot zone. 75×, 2% HF etch.

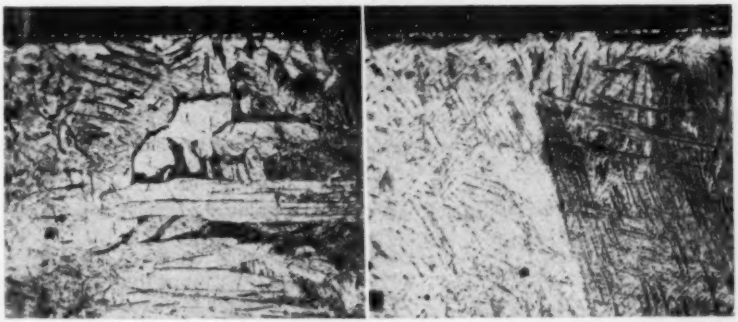

FIG. 7 FIG. 8

FIG. 7-8. Foote Mineral Zr, heat treated in vacuo 1 hr. at 1400°C. with 0.2% oxygen added. 75×, 2% HF etch.

with the abrupt phase change in Fig. 5. With the addition of oxygen, the hardness of the zirconium wire increases rapidly. Here again the increase

becomes apparent only well beyond the phase boundary of Fig. 7. There may have been chance contamination of the first sample. When the sample of Bureau of Mines zirconium was heated, there was little difference in the hardness between the hot section and the cold end. However, in this instance, the transition region of Fig. 10 and 11 is much harder than any other spot.

FIG. 9 FIG. 10

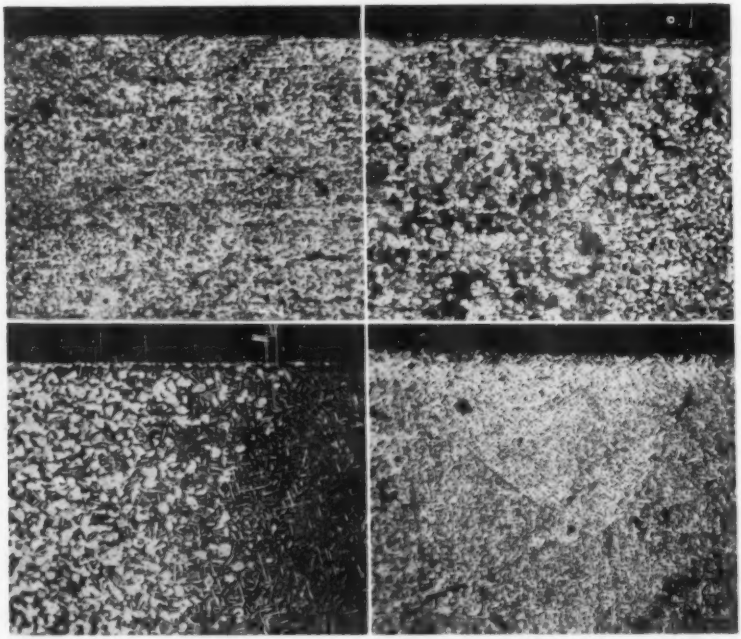

FIG. 11 FIG. 12

FIG. 9–12. Bureau of Mines Zr, heat treated in vacuo 1 hr. at 1400°C., no added oxygen. 75×, 2% HF etch.

Some hardness readings are given in duplicate to show the consistency of readings. In one instance, the area of Fig. 4, hard spots resulted in wide variations in values. The impressions in another, a portion of Fig. 7, were so distorted that even the average value shown in parenthesis is in doubt.

In addition to the figures in Table II, micro-hardness measurements were taken in cross-sections of a series of 0.050 in. (1.27 mm.) diam. zirconium wires which had been doped with small percentages of oxygen. The results shown in Fig. 13 are averages of four to six impressions taken near the surface and about the mid-points of the radius. In some instances, the

wires had cores of some foreign material and the immediate vicinity of the core was very hard. Therefore, all readings at the center were discarded. There was no uniform variation in the other readings which would indicate

TABLE II. *Microhardness of heat treated zirconium*

Distance from end of wire	Microhardness VPN (.1855 kg. load)	Micrograph reference
Foot mineral zirconium heat treated only, 1 hr., 1400°C.		
mm.		
2	93	
4	107	Fig. 3
5	107	
5.5	83, 137	Fig. 4
6	86	
6.5	89	Fig. 5, left to right
7	117	
7.5	102	
8	98	
10	118	
12	134	
16	177	
20	163	Fig. 6
Foote mineral zirconium 0.2% O_2, 1 hr., 1400°C.		
4	91	
5	106	Fig. 3
6	91	
6.5	74	
7	(127)	Fig. 7, left to right
7.5	91, 96	
8.5	112	
10	129	
12	180, 184	
16	208	Fig. 8, each side grain boundary
16.2	197	
20	212	
Bureau of Mines zirconium heat treated only, 1 hr., 1400°C.		
3	232	
5	225	Fig. 9
7	261	Fig. 10
8	280, 310	Fig. 11, left and right
9	222	
10	215	
11	225	
13	240	
16	232	Fig. 12

that the added oxygen was not well dispersed throughout the thickness of the wire. The first point for Foote Mineral wire in Fig. 13 is plotted as nearly zero oxygen content while the second, which is heat treated wire, reflects the average oxygen content of such wire obtained by analysis.

The smoothness of the curve is perhaps in part fortuitous and the probable error in the readings was greater than indicated by the deviation of the points.

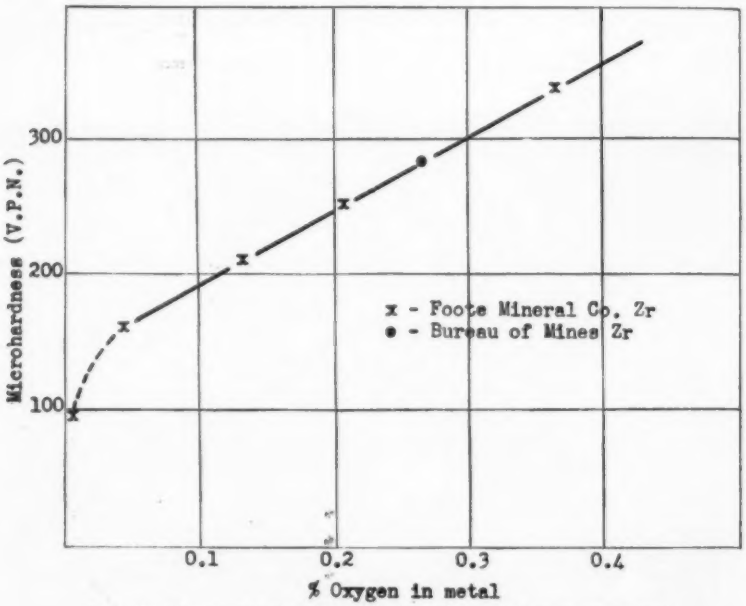

FIG. 13. Increase in hardness of zirconium with oxygen content

SUMMARY

Of the methods described for the evaluation of oxygen in zirconium, it may be generally stated that the indirect method is of value as a control method or where the oxygen content is relatively high and the necessary correction factors are known with certainty.

The direct method shows, with reference to Table I, a precision of approximately .02 per cent oxygen using 2 g. samples for analysis. The accuracy, referring to Table I and Fig. 2, cannot be evaluated with certainty from the limited work done but, in general, it appears that the results are a little low.

The effect of nitrogen on the analytical determination of oxygen is being studied but data are not available. This is important in the analysis of commercial zirconium but has little influence on results reported here, especially on Foote Mineral wires since the nitrogen content is approximately .01 per cent.

The hardness of zirconium is somewhat dependent upon the microstructure of the metal even in well annealed pieces. These is a rapid increase in hardness with increasing oxygen content and it is probable that zir-

conium containing 0.2 per cent dissolved oxygen or more would be cold workable only with difficulty. It is known that nitrogen too increases the hardness of zirconium although to what extent has not yet been determined.

Any discussion of this paper will appear in the discussion section of Volume 93 of the Transactions of this Society.

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REACTIONS OF CARBON AND METAL OXIDES IN A VACUUM[1]

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ABSTRACT

The literature on the reactions of carbon and metal oxides in a vacuum is reviewed and the results of an experimental study of the reduction of several metal oxides by carbon in a vacuum are reported. None of the refractory oxides studied were stable in contact with carbon in a vacuum at temperatures above 1380°C. Oxides of multivalent metals reacted at temperatures of 700°C. or less. As a method for producing pure metals, best results were obtained with chromium, vanadium, columbium, and tantalum. A chromium metal analyzing 97 per cent Cr and a vanadium metal analyzing 93 per cent V were obtained. It is concluded that the vacuum reduction method would be practical only for the production of the more expensive and rare metals.

INTRODUCTION

The successful large-scale commercial application of high vacuum at high temperatures is a comparatively new development in metallurgy The use of the ferrosilicon process for the production of magnesium during the war forced a perfection of high vacuum equipment and techniques that may well open the way for a great expansion of vacuum metallurgy Vacuum operations that were possible only in the laboratory a few years ago are now plant practice. An added incentive for research in this field

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is the existence of the idle government-owned magnesium plants which would be available for the production of other metals.

Many reactions can be promoted by being conducted in a vacuum. This paper deals only with the reduction of metal oxides with carbon or carbides, and was undertaken because the method has been patented for the production of a great many metals, although very little supporting data can be found. The work has shown that there are many difficulties in applying such a method for the practical production of metals and that many of the patent claims are apparently without basis. The investigations have yielded considerable information, however, on the mechanisms of the reduction and the complexities of the conditions that exist with the various metals. The work was carried out at the Northwest Electrodevelopment Laboratory, Bureau of Mines, U. S. Department of the Interior, as a part of a general program for the production of pure metals.

REVIEW OF PREVIOUS WORK

The reaction of carbon with a metal oxide is the oldest method employed for the production of metals, but the use of a vacuum to aid in the elimination of the reaction gases is a fairly recent development. The advantage of using a vacuum is that it shifts the equilibrium reaction:

$$MeO + C \rightleftharpoons CO + Me$$

to the right. Both high temperature and high vacuum influence the reaction in that direction.

The vacuum reaction of oxides with carbon is mentioned quite frequently in technical literature. Von Bolton (18) suggested that the oxide contained in tantalum could be removed by adding a little carbon to the metal and eliminating both the carbon and oxygen as CO in a vacuum at an elevated temperature. Recently Balke (2) stated that pure columbium could be made by heating columbium oxide with carbon in a carbon resistor furnace. The possibility of such a method had been mentioned by Rohn (14) who allowed carbides dissolved in a metal bath to react with an oxide at a high temperature in a vacuum. Rohn's method was said to be suitable for the production of the elements, Si, Ti, Zr, Hf, Th, V, Cr, Mo, and Cb as well as for the production of their alloys with other metals.

The I. G. Farbenindustrie (11) patented a similar method in which the oxide and carbide as solids were allowed to react in a partial vacuum containing a little hydrogen, which they claimed accelerated the reduction to a metal. It was claimed that the process could be used for the production of the metals of the 2nd to the 7th group of the periodic system and of their alloys and to be especially applicable to the metals, Be, Mg, Al, Si, Ti, Th, V, Cb, Ta, Mo, W, U, and Mn. The patent mentions a number of examples, including the production of carbon-free chromium, ferrochromium, and nichrome; the chromium was obtained at 1200°C. at a pressure of 30 mm., but the nichrome required a temperature of only 1000°C. Baukloh (3) and his associates have given data concerning vacuum reactions in the solid state; they examined the reduction of the oxides of Mn, Fe, Ni, Cr, Si, Sn, Pb, Cu, Co, and W by carbon.

The volatility of the products is especially worthy of note because it is a problem encountered in the vacuum reduction of a number of the metals.

If the metal is volatile at the temperature of reduction, the product in the condenser will almost certainly be contaminated with carbide or oxide. Such a result was obtained by Heussler (10) who attempted to produce carbides in a vacuum by heating MnO or SiO_2 mixed with carbon. He found that all of the manganese or silicon had volatilized and condensed as carbide and oxide in the cool end of the tube. The experiment gives the illusion that manganese carbide is volatile, while actually it is formed again from sublimed manganese and CO. In the case of silica, its partial reduction produces the volatile compound SiO described by Potter (20) and by Zintl (19); thus the condensed material in Heussler's experiment probably contained silicon monoxide, silicon, silica, and silicon carbide. Sloman (15) observed the volatility of manganese and its recombination with CO in the condenser when he attempted to degas alloys in a vacuum.

The reaction of CaO and BaO with carbon in a vacuum has been studied by Thomson (16). Using a carbon resistor furnace operating at 1400°C., he found that CO is evolved and calcium oxide condenses on the furnace walls. Some CO reaches the pump, but the rest recombines with the calcium forming carbide-oxide mixtures. The similarity to the carbothermic magnesium process is apparent. The recovery of calcium is complicated by the fact that calcium has a fairly high affinity for carbon so that there is, in addition to the back reaction with CO, also a recombination of calcium with liberated carbon in the condenser which makes reclamation of the calcium rather difficult. Similar difficulties are encountered when beryllia-carbon mixtures are reduced in a vacuum to produce beryllium metal, as patented by Kjellgren (12), and in the reduction of magnesia-carbon mixtures as was pointed out by Watts (21).

Recently Ford, Ensign, and Quinn (6) have proposed the carbon reduction of magnesium in much the same way as recommended in the I. G. Farben patent (11) mentioned previously. The Ford patent suggests that because of the volatility of magnesium, part of the metal could be recovered from the condensate, which is mainly oxide and carbon, by holding the condenser at or above the dew point of the magnesium by controlling the pressure and temperature. The recovery of metals in such a vacuum carbothermic process is a very difficult task since quenching the gases is not always possible.

THEORY OF REDUCTION WITH CARBON IN A VACUUM

When a metal oxide is heated with carbon, carbon monoxide and dioxide form according to the following equation,

$$MeO + xC \rightleftharpoons yCO + zCO_2 + Me$$

Carbon dioxide may react back with carbon to produce more CO, or the CO may react with the metal oxide to form more CO_2. The production of both CO and CO_2 is a considerable drawback in the manufacture of low-carbon or oxide-free metal, since it is difficult to predict how much carbon will stay behind in the metal. CO_2 carries off only half as much carbon per unit of oxygen as does CO. The carbon content in the end product is dependent on the heating rate and on the temperature of the operation.

If a metal oxide is reduced with carbon, a carbide is formed, at least as an intermediary product, by all those metals having a sufficient affinity for

carbon. Therefore, it is worth while to consider the possibility of the reaction of a carbide with oxide. The advantage of the reduction of oxide with a carbide is the greatly reduced evolution of reaction gases which means that less pumping is required. In the equation

$$FeO + C = CO + Fe$$

a given volume of CO is evolved for each unit weight of iron, while in the equation

$$Fe_3C + FeO = 4Fe + CO$$

only one fourth that volume is liberated for the same weight of iron obtained. If a carbide is to be used, a two step process is required, the first step being that of making the carbide at atmospheric pressure, and the second one, the vacuum reduction itself. There is also an advantage in using the lowest possible oxide to react with the carbide so as to limit the amount of gas produced.

The limit of deoxidation of oxides by carbides is governed by the stability of the two compounds. Metals, such as titanium or zirconium, that form the most stable of all known carbides, may not react completely even at the highest temperature to be attained in furnaces and in the best obtainable vacuum.

The studies of equilibria between oxides and carbon, described in the literature, have been confined mainly to the oxides of the more common metals such as iron, zinc, lead, and copper; even for those metals there is not much to be found about reactions in the solid state. Likewise, the equilibria between gases, solid oxides, and metals, which are of great importance in the reduction process, are not determined to any extent. Recent work by Darken and Gurry (5) is devoted to the equilibrium of solid iron, oxygen, and CO-CO_2 mixtures. Herty and coworkers (8) determined that 0.12 oxygen is soluble in iron at 1520°C. Cobb (4), found that only 0.018 per cent CO is soluble in solid iron between 1490° and 1539°C. In general, it can be said that CO does not migrate through iron, but that its constituents do. It is known that CO coming into contact with an iron surface at high temperatures partially dissociates and forms CO_2 and a diffusion layer of steel containing 1.2 to 1.4 per cent carbon.

A study of the oxidation of resistor wires by Hessenbruch (9) is the basis for some surmises as to the mechanism of the diffusion of oxygen into metals. For those metals that dissolve in their own oxides, such as chromium and iron, oxidation at high temperatures takes place at the interface between the air and oxide because the latter contains dissolved metal which is repleted constantly by diffusion from the main metal body. The grain boundaries are the channels through which the oxidation proceeds. As a rule the diffusion of the metal is more rapid in the lower oxide; Tritton and Hanson (17) found that FeO dissolves 1 per cent of Fe.

The sequence described above would be reversed in the reduction in the solid state of a metal oxide with carbon, carbide, or CO. The first metal reduced dissolves in the oxide until the saturation point is reached, then metal particles saturated with oxide separate out. These particles tend to agglomerate with the other particles, if the conditions are right, and the mixture becomes more compact. The coalescence may be so pronounced

that the gases cannot escape and pressure builds up until the reduction is stopped because an equilibrium has been reached. As was stated above, diffusion of the CO through metals does not occur as far as can be determined. An alternative possibility is that the evolution of CO and CO_2 and loss of carbon loosens up the reaction mixture to such an extent that contact between the oxide and carbon particles is lost and the reaction stops. If either of these extremes is reached it is necessary to crush the mixture, rebriquette it, and start the reduction again. As the product becomes more metallic, the coalescence of the particles is greater and it becomes more difficult to eliminate the residual carbon because the reaction gases cannot escape. It is obvious that the production of a pure metal by this method is subject to many interferences.

PROBLEM

The present investigation is concerned with two different aspects of the problem of the reduction of oxides. First, how far does the reduction of certain metal oxides proceed in a vacuum and can a reasonably pure metal be produced. Second, at what temperatures do certain oxides first react with carbon. This latter point is of importance in that it determines the usefulness of oxide refractories in contact with carbon under a vacuum. It is probable that commercial high-temperature vacuum furnaces will employ graphite resistance elements within the furnace to obtain high temperatures in large equipment.

Such an evolution of furnace design has already started. The first plants for the production of magnesium by the ferrosilicon process used externally heated retorts, usually 10 inches in diameter and 7 to 10 feet long. This type of unit had the disadvantages of small capacity and a tendency for the retort walls to collapse at the high temperatures required. An improved type of furnace was developed by the Electrometallurgical Corporation as patented by Bagley (1) and used at the Spokane plant for the production of magnesium. The chief feature is the construction of the heater elements inside the furnace in such a manner that the outside wall of the furnace, which must withstand atmospheric pressure, is not subjected to high temperatures.

The next logical step in furnace construction is the use of heater elements that will give higher temperatures than the 1200°C. obtainable with the usual nickel-chromium alloy wires. Graphite resistors have possibilities although their limitations when used in a vacuum must be recognized as was pointed out in a previous paper (13). Before such commercial graphite resistor vacuum furnaces can be developed, specific knowledge must be obtained about the behavior of oxide refractories in contact with hot carbon or carbon vapors in a vacuum. The results of the investigation being described should have value from this standpoint.

EXPERIMENTAL PROCEDURE

For the experiments described in this paper, two furnaces were used. For temperatures up to 1300°C., a furnace was made of a porcelain tube heated with windings of Smith No. 10 alloy resistance wire coiled on an alundum core. Fig. 1 shows this furnace (12, 13). The furnace was built with the heated zone on top in order that any metal vapors that

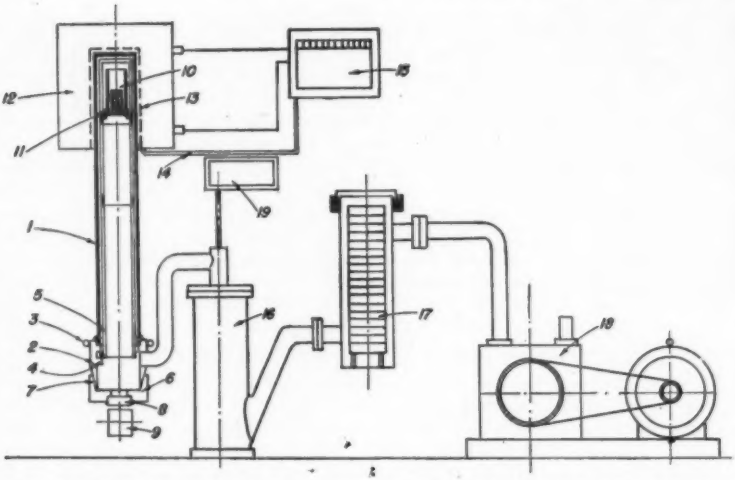

FIG. 1. Resistance vacuum furnace. 1. porcelain tube, 2. conical head, 3. water cooling, 4. bayonet, 5. insert, 6. conical cover, 7. ground joint, 8. glass window, 9. mirror, 10. crucible with batch, 11. bayonet, 12. metallic resistor furnace, 13. smith 10 alloy coil, 14. thermocouple leads, 15. temperature controller, 16. oil diffusion pump, 17. P_2O_5 drying tower, 18. mechanical pump, 19. McLeod tilting gauge.

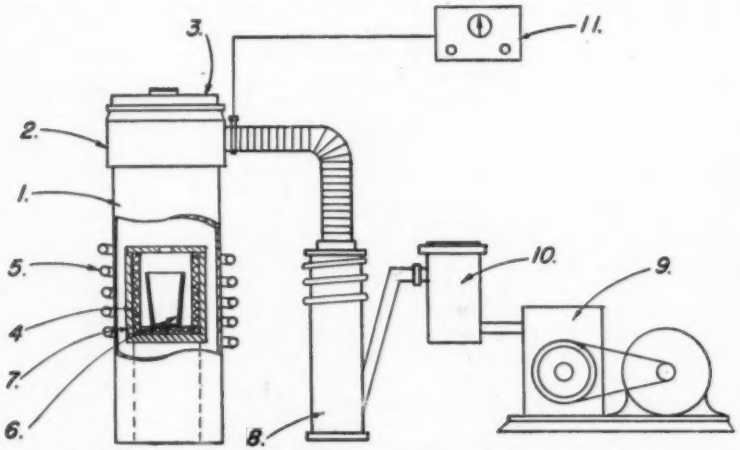

FIG. 2. High frequency vacuum furnace. 1. silica tube, 2. conical head, 3. cover, 4. tungsten rings, 5. work coil, 6. beryllia crucible, 7. beryllia rings, 8. oil diffusion pump, 9. mechanical pump, 10. drying tower, 11. Pirani gauge.

might be formed would be condensed downward. For temperatures above 1300°C., a high frequency furnace (Fig. 2) was used; this furnace readily attained a temperature of 2000°C.

Finely powdered metal oxides of C.P. grade were used for experiment and a sample of common fireclay was also run to determine its refractory properties in a vacuum. The oxide samples were intimately mixed with minus 100 mesh graphite in the proper stoichiometric amounts based on the reduction of the oxide to metal with evolution of CO. The oxide-graphite mixtures were briquetted, weighed, and heated in the resistance vacuum furnace. The temperature was increased slowly and vacuum readings were taken periodically.

The temperature at which the first appreciable gas evolution was obtained was recorded as the beginning of the reaction. This temperature could not be determined with great exactness because small amounts of gas were given off at somewhat lower temperatures. However, the data do indicate when a definite and noticeable breakdown of the mixtures occurs.

The furnace was left at the temperature of the reaction until the gas evolution had ceased and then the temperature was increased slowly to determine if there was a secondary reaction. If the maximum temperature

TABLE I. *Temperature at which metal oxides and carbon first react*

	Under high vacuum	At atmospheric pressure*		Under high vacuum	At atmospheric pressure*
	°C.	°C.		°C.	°C.
V_2O_3	650		SiO_2	1250	1460
Cr_2O_3	690	1105	ZrO_2	1300	1400
La_2O_3	700		CaO	1305	
UO_2	800	1480	BeO	1315	
CeO_2	800		MgO	1350	
TiO_2	1100		Al_2O_3	1350	
Ta_2O_5	1100		ThO_2	1380	1600
Fireclay	1100				
B_2O_3	1200				

* Data taken from Greenwood.

of the resistance vacuum furnace, 1300°C., was not considered sufficient, the briquette was transferred to the induction vacuum furnace and the same heating procedure was followed to much higher temperatures.

After completion of the run, the briquette was removed from the furnace, weighed, and analyzed if the data obtained on heating warranted it. The briquettes in which oxide was reduced to metal were crushed, rebriquetted, and reheated to give opportunity for complete reaction between the oxides and the graphite.

EXPERIMENTAL RESULTS

The data in Table I show the temperatures at which the metal oxide and graphite mixtures first begin to react at an appreciable rate when heated in a vacuum. It can be seen that none of the oxides resist the action of carbon in a good vacuum above 1380°C., the temperature at which ThO_2 begins to break down. Some of the oxides react below 700°C.; these are usually the oxides of multivalent metals which give off their "loose" oxygen atoms and form lower oxides. After the first breakdown, the resulting lower oxides may be stable in contact with carbon to much higher temperature, and,

therefore, could be considered as likely refractory materials. Under some conditions oxygen may coexist with carbon in compounds or solutions that may be very resistant to further reduction. A ready breakdown to lower oxides occurs with the oxides of Cr, U, V, La, Ce, Si, and Ti, while Zr and Th are much more resistant.

As a matter of interest Table I includes results obtained by Greenwood (7) who determined the temperature at which certain oxides started to react with carbon when heated at atmospheric pressure.

In Table II information is given concerning the reaction products obtained when mixtures of metal oxides and graphite were heated in a vacuum.

Of the various metal oxides used in these runs, Cr_2O_3 was reduced with the most success. Heating to 1300°C. gave a product containing 6.3 per

TABLE II. *Reduction of metal oxides with carbon in a vacuum*

Oxide	Max. temp.	Pressure at max. temp.	Weight loss of charge	Carbon analysis			Observation
				Feed	Product	Remelted product	
	°C.	*microns*	*per cent*	%	%	%	
V_2O_5	1550	2	49.0	18.6	2.2	0.76	V = 84.5% (fused)
Cr_2O_3	1460	8	68.0	18.7	0.38	0.09	Cr = 97.0% (fused)
La_2O_3	1300	25	12.8	10.0	10.6		
UO_2	1350	40	21.4	10.2	3.51		
CeO_2	1300	15	6.4	8.3	3.14		Pyrophoric metal
TiO_2	1800	8	73.7	31.0	20.7		Ti = 73.7%
Ta_2O_5	1800	2	25.2	11.9	2.19		
Fireclay	1300	16	30.7	28.5			
B_2O_3	1300	22	75.5	34.0			Residue chiefly C
SiO_2	1300	22	9.0	28.7	22.5		Condensate obtained
ZrO_2	1300	10	3.1	16.4			
CaO	1500	7	42.2	17.6			Ca + CaC_2 in condensate
BeO	1550	100	9.4	32.5			Be in condensate
MgO	1525	6	10.9	23.0			Mg in condensate
Al_2O_3	1550	500	27.5	26.0			Al + Al_4C_3 in condensate
ThO_2	1650	4	17.7	8.3	4.12		
ZrO_2 + ZrC	1980	3	3.7	7.45	6.15		Zr = 83.7%

cent C, but by heating to 1460°C. the carbon content was reduced to 0.38 per cent. When this metal was melted under a helium atmosphere, the carbon content was further lowered to 0.09 per cent. The chromium content of this last material was 97 per cent. Unfortunately, at the reduction temperature of 1460°C. there is considerable volatilization of the metal, as is shown by the weight loss of 68 per cent.

Vanadium reduction

In an attempt to obtain a better vanadium metal a number of additional runs were made. The carbon content of the feed was varied to determine the correct amount for the reaction. However, no definite relationship could be found and all of the metal produced contained some residual carbon.

The temperature was held as close as possible to 1550°C. in the final reduction stage; this was about the maximum temperature that could be

maintained without melting the metal. (See Table III for data.) Melting took place at 1580°C. at which temperature the vanadium had a low vapor pressure.

When the vanadium oxide-carbon mixture ceased to react, it was removed from the furnace, crushed, rebriquetted, and reheated with a new evolution of CO. The final step was to fuse the metal in a beryllia crucible. If the temperature was raised much above the melting point of the vanadium the metal reacted violently with the beryllia.

The data of Table III show that a metal of better than 94 per cent vanadium and about 1 per cent carbon can be made; although the vanadium content may appear low it should be compared with the best commercial vanadium metal which contains only 95 per cent V. Evidently the vanadium metal made in these experiments still retains about 5 per cent of oxygen which can coexist without reacting with the carbon content though the metal is fused in a high vacuum. Unfortunately there is no reliable and easy method for determining the oxygen content of vanadium and it can only be deduced by difference.

TABLE III. *Reduction of V_2O_5 with carbon in a vacuum*

Run no.	Max. temp.	End vacuum	C in feed	Analysis of metal			Observations
				% C	% V	% Si	
	°C.	*microns*	*per cent*				
1	1550	2	18.4	2.20			
Same fused				0.76	84.5		
2	1550	2	16.9	3.64	87.7		
3	1520	2	20.8	2.18	91.0		
4	1550	2	20.8	0.99	93.4	0.06	Recovery of V = 94.5%
Same fused				0.97	94.3	0.07	

Columbium reduction

The reduction of columbium oxide was studied by using a "pure" columbium oxide obtained from a dealer. The conditions of the run were as follows: 53.2 grams of columbium oxide and 9.6 grams of minus 100 mesh graphite were mixed, briquetted, and heated for 36 hours at 1300°C., by which time the vacuum had dropped to 20 microns. The weight loss was 24.8 per cent and the product contained 9.9 per cent carbon. This product was crushed, mixed with enough oxide to eliminate the residual carbon as CO, briquetted, and sintered on a tungsten plate in a carbon resistor furnace at 1920°C. until the vacuum dropped to 2 microns. The product now contained 2.4 per cent carbon. A repetition of this last step was carried out except that the temperature was raised to 1950°C. The product, which was metallic but brittle, was crushed, briquetted, and fused on a thoria layer at 2400°C. in a high frequency furnace. The final analysis was: 79.3 per cent Cb, 19.8 per cent insoluble in HF_2 and 1.01 per cent C.

The insoluble residue had picked up practically no thoria on the basis of geiger counter tests. The metal ingot had a Rockwell B hardness of 80 and could readily be turned on the lathe despite the fact that it seemed to contain free inclusions of oxide.

The results of this experiment indicate that although columbium metal can be produced by such a method, the carbon and oxide do not react completely and a large excess of oxide has to be present to reduce the carbon content to an acceptable figure.

Reduction of other metals

Other metal oxides showed some promise of reduction to a pure metal. A number of runs with readjustment of the carbon and oxide ratio would be required to determine this point definitely. The mixture containing uranium oxide was reduced to 3.5 per cent carbon, but the ingot still showed some oxide. With tantalum oxide plus graphite a carbide was obtained at 1800°C.; oxide was still present. Much higher reaction temperatures would be required to obtain further reduction. Lanthanum oxide could be broken down at 1300°C. to a carbide with 10.6 per cent carbon, but lower carbon contents could be obtained at higher temperatures. Cerium oxide under the same conditions gave a pyrophoric ingot with only 3.14 per cent carbon; the compacts were not fused.

Some of the metal oxides were reduced to metal, but the metal vaporized and was carried over into the condenser where it reacted partially with the gases. This phenomenon was noted with Al_2O_3 heated to 1550°C., MgO heated to 1525°C., and BeO heated to 1500°C.

The results obtained with zirconium oxide and graphite, and with zirconium oxide plus zirconium carbide, indicate that this oxide is not reduced to a metal even at extremely high temperatures, a question which was recently brought up for discussion (2). The carbide-oxide mixture was heated to 1960°C., which is well above the melting point of zirconium, and yet the briquettes contained 6.2 per cent carbon and 63.7 per cent zirconium which would indicate the presence of about 7.5 per cent oxygen. Thorium oxide was not reduced to metal nor was titanium oxide.

The loss of weight of the TiO_2 plus C and the B_2O_3 plus C mixtures would suggest that a volatile lower oxide is formed such as is obtained with SiO_2.

DISCUSSION

The metals may be grouped in the following manner, using the data from these experiments and that available from literature, on the basis of conditions prevailing when their oxides are reduced with carbon in vacuo.

1. Metals volatile at or below reduction temperature:
   Na, K, Li, Ca, Ba, Sr, Be, Al, Mn, Zn, Cd, Mg.
2. Metals reducible below volatilization temperature:
   Cr, V, Cb, Ta, W, Mo, Fe, Ni, Cu, U, Ce, La.
3. Metals forming stable carbides or oxide carbide solutions:
   Zr, Ti, Hf, Th.
4. Metals forming volatile lower oxides:
   Si, B, (Ti).

In the first group, complications are caused by the formation of stable carbonates with the alkali metals. Recombination in the condenser gives oxide-carbide-carbon mixtures with some free metal in the case of Mn, Ca, Mg, Ba, Sr, Be, Al, Li, Na and K. The recovery of the metal in the condenser by quenching would increase the yield, but this is not easy to do in a vacuum.

In the second group, chromium, vanadium, columbium, and tantalum offer the most promise for the production of metal. Unfortunately, the volatilization of chromium is pronounced at 1400°C. so that there are losses by evaporation. Vanadium requires a high reduction temperature of about 1550°C. which is in reach of carbon resistor furnaces. It is possible that a fairly pure vanadium can be made by the vacuum carbon-oxide process. Unreacted carbon and oxide are found in the metals, V, Cb, U and Ce.

In the third group, only carbide-oxide mixtures are produced.

The fourth group gives volatile lower oxides. Depending on the degree of volatility, only a part of the lower oxide may escape as such, while the rest of the metal may combine with carbon to form carbide or carbide oxide mixtures. This appears to be the case with titanium, which volatilizes partly as lower oxide, and partly stays behind as a carboxide.

CONCLUSIONS

In the course of these experiments it was found that no refractory oxide is stable in contact with carbon in a vacuum at temperatures above 1380°C. Oxides of multivalent metals react at temperatures of 700°C. and less, the first oxygen atom forming carbon dioxide with the available carbon. Lower oxides of such metals which have not been examined may be more stable. Refractory oxides, therefore, cannot be used for the construction of carbon resistor furnaces operating at temperatures above 1380°C. without reaction of the refractories with carbon vapor even though they are not in direct contact with the carbon resistor itself.

The vacuum reduction of metal oxides with carbon as a method for producing pure metals is limited in scope. The best results are obtained with chromium, vanadium, columbium and tantalum. A chromium metal with 97.0 per cent Cr and a vanadium metal with 93.4 per cent V was obtained. The former contained only 0.09 per cent C, the latter 0.99 per cent C. The metals silicon, boron, and to some extent titanium are volatilized as lower oxides. Metals such as beryllium, aluminum, magnesium, and manganese are vaporized and recombine in the condenser with the CO. Zirconium and thorium form stable carbides and the deoxidation stops after reaching equilibrium. Owing to the stability of the carbides of columbium and vanadium the end products contain oxides and unreacted carbon.

The main difficulties encountered in reducing oxides in vacuo are those caused by the sintering of the metal. The voids through which the carbon monoxide can escape are sealed, pressure builds up, and the deoxidation stops because the reduction equilibrium, which is pressure conditioned, is shifted to the side of oxide stability. Repeated regrinding and reheating is necessary to obtain high grade metal.

It would seem that this method would be practical only for the more expensive and rare metals and that its success depends on the availability of high vacuum pumps of large capacity.

Any discussion of this paper will appear in the discussion section of Volume 93 of the Transactions of this Society.

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THE DEPOSITION OF TANTALUM AND COLUMBIUM FROM THEIR VOLATILIZED HALIDES[1]

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ABSTRACT

The general conditions for obtaining adherent, ductile, nonporous coatings of tantalum and columbium by hydrogen reduction of their pentachlorides are discussed. Deposits up to 0.030 inch (0.76 mm.) or more in thickness have been obtained on copper, iron, alloy steels, nickel, molybdenum, and ceramic bases at rates up to 0.0003 inch (0.008 mm.) per minute and efficiencies up to 60 per cent. The forms coated include wire, rod, sheet, block, tube, and crucible. Some of the chemical and physical properties of the plates are described, and micrographic and X-ray diffraction studies of a few deposits are presented.

INTRODUCTION

Tantalum and columbium possess a wide variety of useful properties, both physical and chemical, which have resulted in an increasing number of industrial applications of these metals during the last decade, thus rapidly eliminating them from the ranks of the so-called less familiar elements, despite their relative scarcity. Among the more important properties of tantalum and columbium are their high melting points, resistance to chemical or atmospheric corrosion at moderate temperatures, low-temperature ductility, high-temperature strength, pronounced anode passivity, excellent gettering qualities, and low secondary electron emission.

The chemical reactivity of tantalum and columbium are quite similar and both have excellent corrosion resistance. The corrosion resistance of

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tantalum is, however, in general, somewhat superior to that of columbium. Because of its almost unique corrosion resistance, the use of tantalum-coated apparatus in many chemical operations offers interesting possibilities. Such a product would permit conservation of the metal and would supplement solid tantalum in applications where the latter cannot be readily used because of fabrication difficulties

Although extremely thin tantalum coatings may be obtained by electrolysis from fused salt baths, no really satisfactory process for obtaining a tantalum or columbium electroplate is known. Fortunately, however, the halides of tantalum and columbium are volatile at moderate temperatures and can be readily decomposed at the surface of a body to be coated to form comparatively thick, adherent plates of the respective metals. The decomposition of halides may be carried out either by straight thermal decomposition or by hydrogen reduction, but the latter process is ordinarily used since it can be carried out at lower temperatures.

As early as 1907, the reduction of tantalum chloride with hydrogen was used by Pirani (1) to coat refractory wires with tantalum and, since that time, considerable use has been made of this and similar vapor-deposition processes, particularly by the lamp industry. However, this work has been almost entirely confined to the coating of wires.

The first extension of these processes to the tantalum plating of larger bodies, that has come to our attention, was carried out by Gonser and Slowter (2) who used the hydrogen reduction process to line nickel tubes and to coat some copper products with tantalum. Although initial results were quite gratifying in that ductile, adherent, and nonporous coatings were obtained, the need for a comprehensive investigation of the plating variables was evident. This investigation was undertaken in 1938 at the Battelle Memorial Institute under the Sponsorship of the Fansteel Metallurgical Corporation of North Chicago, Illinois.

In the course of this work, the tantalum plating process has been extended to the coating of a wide variety of samples, including tubes, pyrometer wells, rocket nozzles, crucibles, slugs, sheet, rod, and wire. The coatings have been applied not only to metals such as iron, copper, nickel, steel, and molybdenum, but to materials such as quartz, alumina, and graphite as well.

The present paper outlines the conditions under which tantalum and columbium can be deposited on the above materials and discusses briefly the applications of this process as developed in the course of the above work.

LITERATURE SURVEY

Reports on the vapor deposition of tantalum prior to 1939 have been reviewed by van Arkel (3) and a brief review of past work on the vapor deposition of metals in general, including tantalum, has been prepared by Maxwell (4).

One of the earliest reports of the preparation of tantalum vapor plates was Pirani's patent on the hydrogen reduction of $TaCl_5$ vapor on a tantalum wire. The tantalum deposit so obtained contained considerable hydrogen, requiring vacuum annealing to produce a pure ductile metal.

Hydrogen embrittlement was avoided in the preparations of van Arkel (5) and Burgers and Basart (6) who thermally decomposed columbium and

tantalum pentachlorides in a vacuum on tungsten filaments heated to 1800° to 2000°C.

Moers (7) found that ductile tantalum deposits could be obtained from a hydrogen-tantalum pentachloride mixture if a filament temperature of 1200°–1450°C. was used. He prepared tantalum rods up to 3.5 mm. diameter at a deposition rate of 3.9 mm. per hour on a 0.05 mm. diameter tungsten core. Columbium deposited under similar conditions was not so ductile as the tantalum deposits (columbium having a greater affinity for hydrogen) (11), but was rendered more ductile by vacuum annealing.

Moers (8) has patented a process for continuously coating wires with refractory compounds and metals, including tantalum. The heated wire is drawn through an axial hole in briquetted chloride, which is vaporized and decomposed either by hydrogen reduction or by thermal decomposition. An apparatus for similarly coating wires in a vacuum has also been patented (9).

PREPARATION OF THE PURE HALIDES

Most of the plating work reported here was carried out with tantalum pentachloride and columbium pentachloride although the pentabromide and pentaiodide of tantalum were used in a few tests. The chlorides were prepared by (a) passing chlorine over heated carbon-oxide mixtures; (b) by passing helium saturated with carbon tetrachloride vapor over the heated oxides; (c) by chlorination of the metals. The last method proved to be the most satisfactory for obtaining large amounts of chlorides and also produced the purest products. Tantalum pentabromide was prepared by bromination of the metal powder, and an impure tantalum pentaiodide was prepared by distilling the bromide in a stream of dry hydrogen iodide.

DEPOSITION PROCESS

The hydrogen reduction of the pentachlorides of tantalum and columbium was used almost exclusively in this investigation since the reduction processes can be carried out at much lower temperatures than the thermal decomposition process and are, therefore, applicable to a wider variety of base materials. The bromides serve equally as well as the chlorides as a source of the metals, but the latter are easier to prepare and are less expensive.

Although the equipment and plating conditions used in plating different types of samples may be quite different, the general process is the same in each case. Purified hydrogen is passed over the chloride powder, which is heated to the temperature required to give the proper partial pressure of the chloride vapor, and thence over the heated article to be coated.

Mechanism of the Deposition Reactions

On metal bases, deposition normally occurs in two stages:

(a) Formation of a thin displacement coating (usually less than 0.0001 mm.) by reaction of the surface metal of the base with the metal halide vapor.

(b) Deposition of the heavier main coating by hydrogen reduction. Under certain conditions, the hydrogen reduction process may proceed wholly or in part to a lower chloride stage, with the resultant nonvolatile subchloride condensing in the cooler portions of the apparatus.

The formation of a displacement coating is indicated in several ways:

(a) Compounds of the base metal, or a thin layer of the base metal itself formed by their reduction, may collect on the walls of the apparatus during the plating process.

(b) In the early deposition stages with some metals, a decrease in the weight of the base metal occurs. Rapid compensation for this decrease results when the hydrogen reduction stage takes place.

(c) Two-layer deposits, in which an extremely thin, adherent tantalum coating on the base is overlaid by a thicker, nonadherent coating, are sometimes obtained. These have been noted on copper bases where no alloying of the base with the coating has ever been detected.

(d) Very thin deposits have been obtained from tantalum chloride-helium or columbium chloride-helium atmospheres under conditions where thermal decomposition does not take place.

On inert bases such as glass and porcelain the only plating reaction is that of hydrogen reduction.

Columbium and tantalum are deposited under similar conditions and can be readily co-deposited by using a plating atmosphere containing the vapor of both pentachlorides. Composition of the alloy plated can be varied according to the respective ratios of the volatilized salts.

Effect of temperature

Deposition sets in at about 600°C. at a very slow reaction rate. The velocity increases with increasing temperature, becoming very rapid at 1400°C. The temperature used is dependent upon the nature of the base and the type of plate desired. Copper articles which must of necessity be plated below 1100°C. because of their low melting point, are usually plated at temperatures from 800°C. to 1000°C. Nickel, on the other hand, may be tantalum plated at temperatures up to 1400°C., i.e., above the melting point of the Ni-Ta interfacial alloy layer. Iron has been plated at temperatures over 1200°C., and molybdenum at temperatures up to 1500°C. The usual temperature range is 900° to 1200°C.

The specimen temperature has a very pronounced effect upon the nature of the deposit. At low temperatures, the deposits are very fine grained, almost amorphous. Raising the deposition temperature causes formation of a more coarsely grained deposit. At very high temperatures, single-crystal deposits have been obtained when a single crystal base has been used (7).

Accompanying this tendency to coarse crystal growth at higher temperatures is the tendency to the formation of nonadherent powder deposits. This does not occur so much in plating small objects as with large ones of extended surface, especially when coating the inside of long tubes. In the latter cases, the gas mixture may be heated sufficiently at the higher specimen temperatures to cause reduction of the chloride to occur at a considerable distance from the surface.

Effect of gas flow

The rate of gas flow past the sample, and whether it is streamline or turbulent, affects the appearance of the plate, its uniformity, and the efficiency of the plating process as measured by the ratio of tantalum deposited to

tantalum in the volatilized chloride that flows through the equipment. Although no special effort was made to obtain high plating efficiencies, values upwards of 60 per cent were observed with low flow rates in tantalum plating wires by a continuous-flow process Additional work on plating other metals by the same process indicates that even higher efficiencies are possible. Higher gas flow rates tend to give brighter, more uniform deposits, but lower efficiency.

Another cause of uneven plating is the edge effect whereby the metal deposits at a much faster rate on sharp edges, points, or sharply curved surfaces. This results in rough, macrocrystalline deposits (many times thicker than the plate on plane surfaces) along the edges and corners of a specimen. The excess metal is easily polished or ground off, however.

The deposition rate increases with temperature and (within certain limits) with the chloride concentration. In the work at Battelle, tantalum deposition rates of up to 0.008 mm. per minute have been obtained on large specimens. Moers (7) reported a rate of 0.06 mm. per minute on wire.

PROPERTIES OF THE COATING

Freedom from porosity

The required thickness of the plate is usually determined by the use to which it is subjected. Deposits varying from less than 0.002 mm. to 0.75 mm. or more in thickness have been prepared in this laboratory, while Moers (7) reported deposits up to 1.7 mm. thick. For corrosion resistance in chemical wear, 0.01 mm.-to 0.06 mm.-thick coatings are normally required since it is difficult to avoid porosity in thinner coatings. Porosity can be eliminated by applying two or three overlapping plates, burnishing each coat, and shifting the specimen within the plating apparatus before applying the next plate so as to cover up pores and avoid nonuniform plating. Using this technique coatings have been obtained which offered complete protection to copper and steel bases against attack by nitric or hydrochloric acid over test periods of 2 to 3 months.

Adhesion and ductility

Coatings 0.1–0.2 mm. thick are applied where mechanical strength is desired. The thicker coatings can be applied in one step or as overlying thin layers. Excellent adhesion and ductility have been obtained in coatings up to 0.1 mm. thick, with the optimum in these properties appearing in 0.04–0.06 mm.-thick deposits. Three-mm.-diameter steel rods with coatings 0.04–0.06 mm. thick were bent repeatedly through angles greater than 30 degrees until failure with no cracking or flaking of the deposit. Coatings with such a high degree of ductility and adhesion have not as yet been obtained in thicknesses greater than 0.1 mm.

In certain instances the physical properties of the base deteriorate greatly during the plating process. Thus, when plating copper, the use of oxygen-free copper is necessary if the embrittlement which ordinary commercial copper undergoes when heated in hydrogen is to be avoided.

The lack of ductility and adhesion in tantalum plates is attributed to the following factors:

(1) Slight hydrogen absorption during the plating and cooling (in

hydrogen) process, especially if a low plating temperature and a long cooling period are used.

(2) Absorption of traces of nitrogen, oxygen, or other impurities from the plating or annealing atmospheres. (The use of impure tantalum pentachloride which contains oxychloride compounds is very detrimental in this respect.)

(3) Absorption of occluded hydrogen or other gases liberated by the base metal during the plating operation. (Nonadherent, brittle deposits were obtained on iron which was previously heated to a red heat and cooled in hydrogen.)

Surface contamination of the base might cause similar results, although the base tends to be self-cleansing during the initial displacement coating reaction.

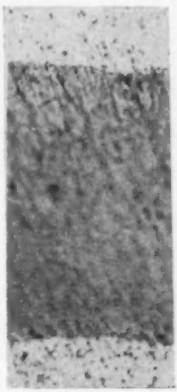

FIG. 1

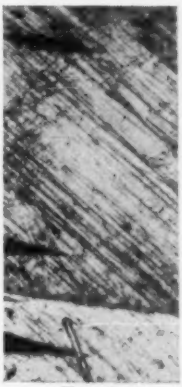

FIG. 2

FIG. 1. Tantalum plate on 1.8 mm.-diameter OFHC copper wire. Unetched 1000×.

FIG. 2. Tantalum plate on high-purity iron. Unetched. 250×.

Hardness

The Knoop hardness numbers obtained for tantalum deposits on copper and iron varied from 220–270, while those obtained for commercial tantalum rod or sheet varied from 60–100.[2]

The ductility of these coatings does not necessarily vary as their hardness, some of the softer coatings being more brittle. The excessive hardness of these plates indicates the presence of a contaminant which is not removed by the annealing treatment.

Structure

A micrographic study of typical tantalum deposits on several bases is presented in Fig. 1 to 3. No alloy layer appears between the unetched copper

[2] No correlation has been obtained between the Knoop hardness numbers and other hardness values for these coatings, but Knoop hardnesses are of the same order of magnitude as the Vickers or Brinell hardness, the Knoop generally being about 20 per cent higher.

base and the tantalum plate in Fig. 1. A number of other micrographs of tantalum-on-copper deposits prepared by different methods likewise show no alloy formation. In Fig. 2, a hard alloy layer appears indistinctly at the tantalum-iron junction as shown by the impressions made by the Knoop indenter. A relatively thick alloy layer appears between the nickel and tantalum in Fig. 3. The alloy is extremely hard and corrosion resistant, and furnishes a very firm bond between the base and the plate. For this reason a flash nickel electroplate is sometimes given to alloy steels, especially those of high chromium content, before tantalum plating to avoid the non-adherent deposits frequently obtained on these metals.

While only one intermediate phase appears in the nickel-tantalum alloy layer in Fig. 3, the formation of Ni_3Ta, Ni_5Ta_3, $NiTa$, and $NiTa_2$ has been reported.

An X-ray diffraction pattern study of tantalum deposited on copper, iron, and molybdenum bases, by hydrogen reduction of the pentachloride at

FIG. 3. Tantalum plate on nickel. Unetched. 750×.

moderate temperatures, has shown the deposited metal to possess invariably a more or less expanded tantalum lattice. This distortion is probably caused by hydrogen held in interstitial solid solution. It was not removed by vacuum annealing at 1200°C. The low-temperature tantalum deposits showed a very severely distorted tantalum lattice, and a fine-grained, virtually amorphous, metal. The extreme lattice distortion is probably caused by the excessive hydrogen absorption which would occur at lower temperatures. It was partially removed by vacuum annealing at 1200°C., which also caused grain growth within the deposit. Tantalum deposits made at higher temperatures showed a less severely distorted lattice and coarser grained metal. Vacuum annealing at 1200°C. had no effect on the internal structure of these plates.

No evidence of alloy or solid solution formation could be found in the diffraction patterns of tantalum deposits on iron and molybdenum bases.

CONCLUSIONS

Procedures and equipment have been worked out whereby a wide variety of products and materials have been successfully coated with tantalum or

columbium by hydrogen reduction of the volatilized chlorides at the surface of the heated material to be coated. Most of the work has been carried out as a batch process, but wire up to 1.5 mm. diameter has been coated by a continuous-flow process, and equipment has been designed for coating pyrometer wells and crucibles in continuous operations.

In addition to wire, rod, tubing, and strip, numerous articles such as pyrometer wells, die blocks, nozzles, and crucibles have been coated with minor modifications in equipment and procedure. Thus, the general method, which has been described in some patents and German technical literature as applied to the coating of wire, has been extended to the coating of other products.

Adherent, nonporous deposits have been obtained on copper, nickel, iron, molybdenum, tantalum, and a variety of alloy steels as well as on graphite, quartz, alumina, and other ceramic bodies. Alloys of tantalum and columbium have been deposited from volatilized mixtures of the pentachlorides of these metals.

ACKNOWLEDGMENT

The authors with to express their appreciation to the Fansteel Metallurgical Corporation for sponsoring this industrial research, and to Dr. W. M. Shafer of that company for his assistance in preparing and interpreting the X-ray diffraction studies.

Any discussion of this paper will appear in the discussion section of Volume 93 of the Transactions of this Society.

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PHYSICAL AND ELECTRICAL PROPERTIES OF CALCIUM[1]

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ABSTRACT

New determinations of the physical and electrical properties of calcium were made for comparison with values given in the literature. High-purity calcium was melted and cast into a slab in an atmosphere of argon gas. The slab was cut into bars which were rolled into sheets and rod without annealing during the rolling operations. Specimens of both sheet

[1] Manuscript received February 7, 1948. This paper prepared for delivery before the Columbus, Ohio Meeting, April 14 to 17, 1948.

and rod were annealed later for certain of the physical and electrical tests. For equal dimensions, the electrical resistance of calcium is roughly 2.6 times that of copper and 1.6 times that of aluminum; and for equal weights

FIG. 1

and lengths, calcium has roughly half the resistance of copper and is equal to that of aluminum. Cold-working hardens the metal very appreciably.

EXPERIMENTAL

Metallic calcium of a high degree of purity was prepared by reducing lime with aluminum in a vacuum and redistilling the condensed product. As the values in the literature for the physical and electrical properties show considerable variance, new determinations were made on this material.

For this purpose, the crystalline product produced by the redistillation process was remelted in a stainless steel crucible and cast into a slab, 3 inches (7.62 cm.) by 8 inches (20.32 cm.) by $\frac{3}{4}$ inch (1.9 cm.), in a stainless steel mold. Both of these operations were carried out in an argon atmosphere of 99.8 per cent purity argon. The slab was cut into bars $\frac{3}{4}$ inch (1.9 cm.) square by 8 inches (20.32 cm.) long and these were rolled into rods $\frac{1}{4}$ inch (0.632 cm.) in diameter, and sheets of $\frac{1}{16}$ inch (0.159 cm.) and $\frac{1}{32}$ inch (0.08 cm.) thickness without annealing. These operations were done in the cold, but samples for tests in the annealed condition were prepared from the product by heating for one half hour at 400°C. in argon. The appearance of the material from which the test specimens were prepared is shown in Fig. 1. Figures 2 to 5 are microphotographs of the slab as cast (2), after reducing the slab to 35 per cent of its original thickness and annealing (3), unannealed rod (longitudinal section) (4), and annealed rod (transverse section) (5).

The chemical analysis of the cast material follows:

	Per cent found	Method of analysis
Calcium	99.48	Hydrogen evolution Titration of oxalate
Iron	0.045	Cupferron
Manganese	0.0025	Bismuthate
Nickel	0.03	Dimethylglyoxime
Chromium	0.004	Colorimetric
Silicon	<0.002	Gravimetric (perchloric dehydration)
Aluminum	<0.01	Colorimetric
Nitrogen	0.032	Kjeldahl
Carbon	0.030	Combustion
Hydrogen	0.012	Vacuum fusion
Oxygen	0.16	Vacuum fusion

The physical properties of the rods, $\frac{5}{32}$-inch (0.397 cm.) diameter by $3\frac{7}{8}$-inch (9.84 cm.) long, are:

	As-rolled, avg. of three	Annealed, avg. of three
Yield, psi	12,300 (865 kg./sq.cm.)	1,990 (140 kg./sq.cm.)
Ultimate, psi	16,700 (1174 kg./sq.cm.)	6,960 (490 kg./sq.cm.)
Elongation in 1 inch (2.54 cm.), %	7	51
Reduction of area, %	35	58

The Rockwell hardnesses, using a 15-kg. load on a $\frac{1}{16}$-inch (0.159 cm.) ball, are 42 as-rolled and too soft to be readable when annealed.

The Erichsen values on the $\frac{1}{32}$-inch (0.08 cm.) sheet are 3.55 to 3.60 as-rolled and 11.1 when annealed.

The electrical resistivities at 70°F. (21.1°C.) are 4.24 minimum, 4.50 maximum, and 4.37 average microhms per centimeter cube as-rolled; and 4.04 minimum, 4.11 maximum, and 4.10 average microhms after annealing. Electrical resistivities were determined on each of six rods at four different currents and the results averaged.

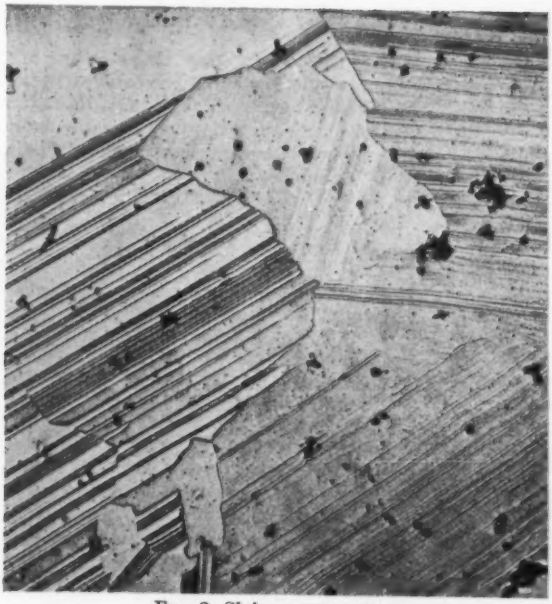

FIG. 2. Slab as cast. 100×

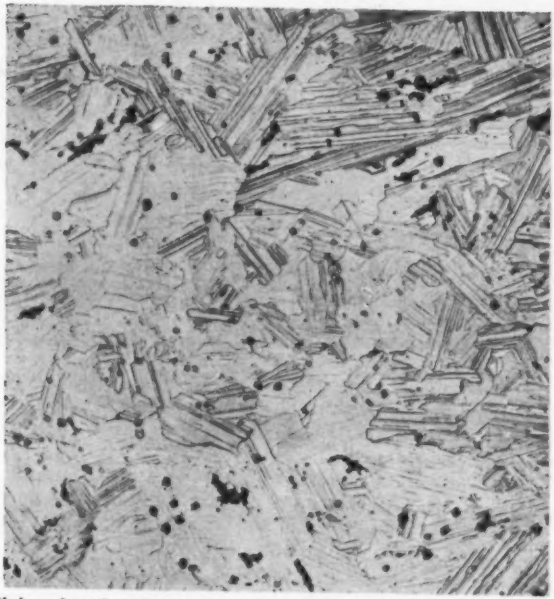

FIG. 3. Slab reduced to 35 per cent of original thickness and annealed. 100×

FIG. 4. Unannealed rod, longitudinal section. 100×

FIG. 5. Annealed rod, transverse section. 100×

For equal dimensions, the specific and relative resistances in comparison with copper, aluminum, and sodium follow:

	Specific resistance	Relative resistance
International annealed Copper standard	1.724	1.00
Calcium	4.53	2.63
Aluminum	2.83	1.64
Sodium	4.8	2.79

For equal weights and lengths, the relative resistance values are:

	Density	Relative resistance
Copper	8.92	1.00
Calcium	1.55	0.46
Aluminum	2.70	0.50
Sodium	0.97	0.30

Corrosion

Specimens of $\frac{1}{16}$-inch (0.159 cm.) sheet and $\frac{1}{4}$-inch (0.635 cm.) rod, as-rolled and annealed, were exposed to the atmosphere but protected from rain and wind during the summer of 1947. After a period of 6 months, the sheet had corroded through in small areas but still maintained a paper-thin foil of metal at the center and approximately full size of the original sheet. Corrosion appeared to have progressed at a uniform rate from both surfaces. The rod showed approximately the same depth of corrosion as the sheet and no difference could be detected between the unannealed and the annealed specimens.

Commercial electrolytic calcium in the form of a cast slab, 2 inches (5.08 cm.) thick, exposed to the atmosphere under similar conditions, corroded to depths of $\frac{1}{4}$ inch (0.635 cm.) in 6 months' time.

CONCLUSIONS

In comparing these results with values previously reported in the literature, no direct conclusions can be reached in most cases because the composition and treatment of the samples are not given in detail. The physical properties are of the same order of magnitude as other published values, but there is a wider range between the as-rolled and annealed conditions, probably due to a larger amount of cold-work on the samples reported here. The electrical resistivity is about the same as that reported in the International Critical Tables (1) (4.60 in vol. 1 and 4.27 in vol. 6 at 20°C. for 99.97% calcium) but is considerably higher than a value on less pure material which was reported by J. H. Goodwin (2) (3.43 microhms/cm.^{3} at 0°C. for 98% calcium). No explanation for this discrepancy could be found from the information given in Goodwin's paper.

As all of the properties included in this report have been checked on a number of specimens of the same composition with little variation in the

results, it is believed that these are reliable figures for calcium of the type described.

Any discussion of this paper will appear in the discussion section of Volume 93 of the Transactions of this Society.

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THE PREPARATION AND PROPERTIES OF PURE TITANIUM[1]

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ABSTRACT

Ductile titanium of high purity is produced by decomposing titanium iodides, formed by the action of iodine vapor upon the crude metal, on a hot filament. The construction and operation of glass units producing 300 to 600 grams of titanium per run in the form of rods of 0.3–0.4 inch diameter are described. This metal has a hardness of about 90 Vickers as deposited, and it can be cold worked drastically by swaging or rolling. Working and mechanical properties have been investigated.

INTRODUCTION

Although titanium is an abundant element, and a number of its compounds have extensive commercial application, the metal itself is available commercially only in very small quantities and in a relatively impure state. This is the result of the very great affinity that titanium has for oxygen and nitrogen, both of which are absorbed irreversibly and which, even in very small percentages, render the metal extremely brittle and hence of little utility.

Since 1910, when Hunter (1) first announced the preparation of malleable lumps of titanium, the preparation of ductile titanium has been attempted by numerous processes. The first successful preparation of the ductile metal was carried out by Van Arkel and de Boer (2) some 15 years later. By using the "iodide process" now familiarly associated in this country with zirconium, they obtained a product that could withstand extreme cold reductions.

In the iodide method, which serves as an agglomeration process as well as a refining process, crude, nonductile titanium is reacted with iodine in an evacuated vessel to form volatile iodides which are decomposed on a heated body, e.g., a tungsten or titanium filament, to form a coherent mass of titanium and liberate the iodine, which resumes its function as a carrier. The success of this process in producing the pure metal from crude metal

[1] Manuscript received March 22, 1948. This paper prepared for delivery before the Columbus, Ohio Meeting, April 14 to 17, 1948.

containing large quantities of oxygen and nitrogen lies in the fact that neither the nitrides or the oxides are attacked by iodine at the temperatures to which the crude metal is heated, and hence they are not transferred.

In the past few years, the Bureau of Mines (3, 4) has made excellent progress in preparing ductile titanium by sintering powder obtained by the Kroll (5) process, i.e., by magnesium reduction of the tetrachloride. However, despite the progress that has been made in the preparation and fabrication of the magnesium-reduced product, the iodide process still offers the most satisfactory means for the preparation of metal of the high purity desirable as a basis for fundamental work on the properties of titanium and its alloys. With this objective, the preparation of high-purity titanium by the iodide process, and an investigation of its physical properties and working characteristics were undertaken at Battelle Memorial Institute under the Sponsorship of the Remington Arms Company, Incorporated.

This paper describes the process used at Battelle in the preparation of iodide-titanium and presents data on some of the physical properties and working characteristics of the metal.

EXPERIMENTAL

Description of apparatus

Vacuum bulbs 100 mm. in diameter were used in initial work but larger units $7\frac{3}{8}$ inches in diameter are now used. A typical bulb unit is shown in Fig. 2. The bulb, itself, is approximately 35 in. long and has a 60 mm. collar to which an electrode cap containing four $\frac{1}{4}$ in. tungsten electrodes is sealed.

A punched molybdenum retainer (Fig. 3) permits uniform distribution of titanium throughout the bulb (see Fig. 2) and also serves as a radiation shield.

Auxiliary equipment includes a nichrome-wound furnace which is used as an annealing oven as well as an operating furnace, a general-purpose vacuum system containing an oil-diffusion pump and a Cenco Hy-Vac pump, and electrical equipment for obtaining, regulating, and measuring currents from 0.5 amp. to 300 amp. A coil of $\frac{1}{4}$ in. copper tubing with a series of $\frac{1}{32}$ in. holes directed towards the furnace walls is included in the furnace to permit air cooling of the bulb during the later stages of the run.

Procedure

The procedure used in preparation of the metal is as follows:

1. The bulbs are loaded with crude titanium metal ($\frac{1}{4}$ in. to $\frac{1}{2}$ in. fused lumps), approximately 13 pounds of metal being required to load the larger unit just described.

2. Tapered tungsten leads consisting of a series of hairpins of 20 mil tungsten wire are fastened to the electrodes with 7 mil molybdenum wire, and a 3 mil tungsten filament is tied to loops at the bottom of the tapered leads. Two hairpin filaments, 24 in. long and 48.5 in. over-all length, are used.

3. To provide proper spacing and suspension of the filaments, they are hooked with 20 mil tungsten wires to an assembly consisting of a molybdenum ring weighted with a block of tungsten and insulated from the tungsten hook by small quartz tubes.

4. The filaments are then carefully lowered through the collar of the bulb and the electrode cap is sealed to the collar. The bulb is then

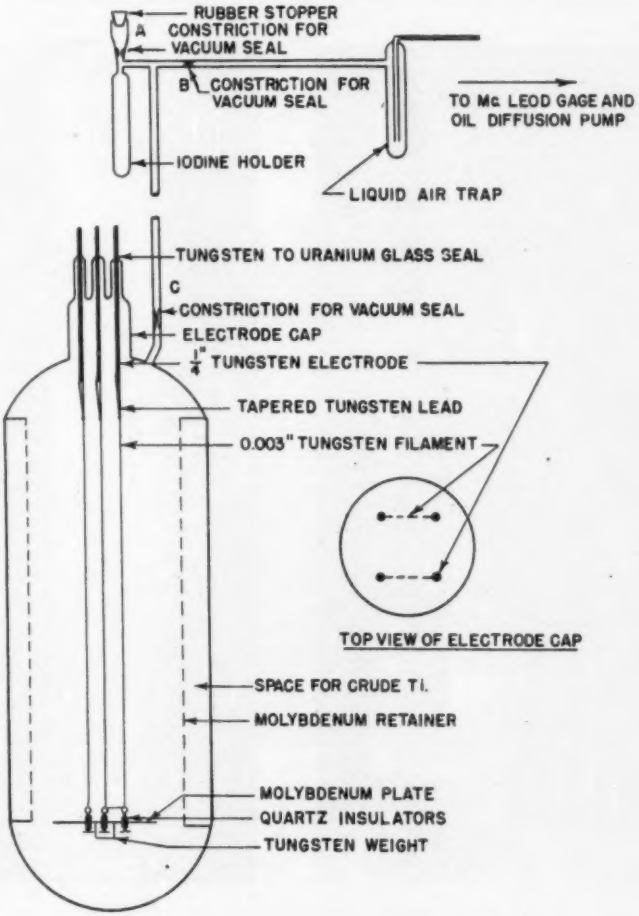

FIG. 1. Schematic diagram of equipment used in producing iodide titanium

evacuated, checked for leaks, and sealed to the vacuum system as shown in Fig. 1.

5. The entire assembly is evacuated and the bulb heated to 525°C. for at least four hours to anneal the glass and to remove adsorbed and absorbed gases. (This operation serves an additional purpose in that the surface

film on the titanium diffuses into the metal, and hence the activity of the titanium is markedly increased.)

6. After the annealing and outgassing operation, the bulb is permitted to cool to room temperature and helium is admitted through a liquid-air trap.

FIG. 2

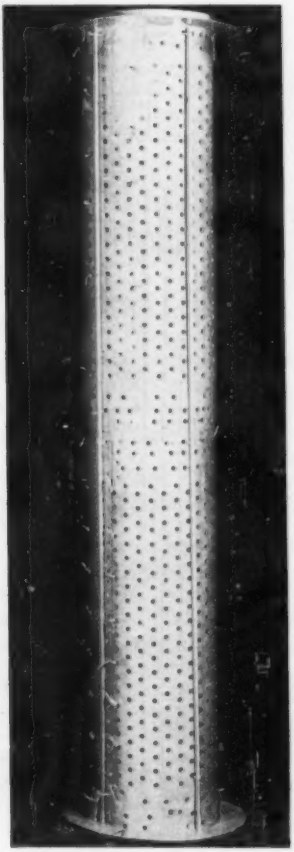

FIG. 3

FIG. 2. Large $7\frac{5}{8}$ in.-diameter deBoer bulb used in production of two 24 in. titanium hairpins (300 g. each)

FIG. 3. Molybdenum retainer used to support crude titanium

7. A weighed quantity of iodine (100–300 g.) is added at (A) while a counterflow of helium is maintained through the inlet. The open end of the iodine container is then sealed off, the iodine is chilled in a dry ice-alcohol bath, the unit again evacuated to 10^{-4} mm., and then removed from the vacuum system by closing the constriction at (B).

8. The iodine is driven into the bulb with a soft flame and a second seal made at (C), approximately one foot from the shoulder of the bulb.

9. The bulb is then suspended in a nichrome-wound furnace and heated to the desired operating temperature (175°C. or 525°C.) overnight in order to insure completion of the reaction between the iodine and the crude titanium.

10. Deposition is initiated after the above incubation period by heating the filament to 1300–1400°C. The temperature of the filament is regulated by controlling the filament current, and is determined optically, corrections being made for the absorption due to iodide vapor and for the emissivity of titanium.

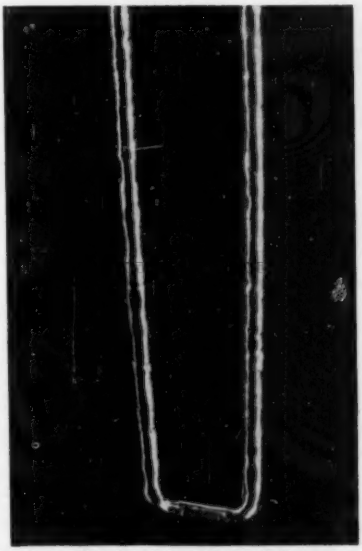

FIG. 4. Hairpin of titanium obtained by thermal decomposition from the iodide

For a final filament current of 250 amp., the titanium bars are approximately $\frac{1}{3}$ in. in diameter, and the capacity of the unit shown in Fig. 2 is approximately 600 g. at a 175°C. bulb temperature. A typical titanium hairpin is shown in Fig. 4.

DISCUSSION OF THE DEPOSITION PROCESS

The general principles of the iodide process have been outlined in the introductory section. As indicated there, the success of the process in producing ductile metals results from the failure to transfer oxygen, nitrogen, or carbon. Because very small quantities of oxygen, nitrogen, or carbon impair the ductility of titanium, and the material produced by the iodide process has such exceptional ductility, it is frequently and mistakenly assumed that iodide-titanium is necessarily of very high purity.

This is, however, not necessarily true since a number of impurities, notably silicon, boron, iron, aluminum, and beryllium can be transferred. In addition, zirconium, hafnium, and thorium will be present in the final product if present in the crude metal. However, other metals such as chromium and tantalum which may be prepared also by the iodide process, but whose iodides are less volatile or less stable, are not transferred at the bulb temperature used in this work.

It should not be thought that a wholesale transfer of the above impurities takes place, however. Actually the percentage transfer is low in almost every case and the above discussion applies to presence of minor quantities of these impurities in the final product, and they can be eliminated, in any event, by the use of crude metal free of the above contaminants.

Titanium deposition can be carried out over two ranges of bulb temperatures, and the bulb temperature influences the transfer of impurities. The exact temperature ranges which may be used are determined by the particle size, surface condition, and purity of the crude titanium which govern its relative reactivity toward iodine and titanium tetraiodide.

With fused titanium, or material of low porosity, bulb temperatures of 50–250°C. give a reasonable rate of deposition from the tetraiodide if lump titanium is used. Over this temperature range, the reaction between the crude titanium and the tetraiodide to form the less volatile diiodide is relatively slow, hence the time required to tie the iodine as the diiodide is sufficiently great to permit completion of the deposition process. At temperatures below 50°C. the reaction between the iodine and the crude metal is too slow to give satisfactory deposition rates, although Fast (6) has indicated that deposition can be obtained in bulbs maintained at room temperature. At temperatures from 250–450°C., the deposition rate falls off markedly due to the rapid formation of the diiodide which is not volatile at those temperatures. At higher temperatures, deposition can be obtained, the diiodide being sufficiently volatile to provide adequate deposition rates. It should be pointed out that the di- and triiodides of titanium readily disproportionate, however, and these disproportionation reactions influence the overall deposition reactions. The triiodide, in particular, undoubtedly contributes to the deposition, particularly at the higher bulb temperatures.

No differences have been observed in the nature of the deposits obtained at the two bulb temperatures (175°C. and 525°C.), but there is a difference in the transfer of impurities. At the lower bulb temperatures, the deposited titanium may contain up to 0.1 per cent iron where the crude titanium contains 1 per cent iron but, at the higher bulb temperature, the ferric iodide is sufficiently unstable that any transfer of iron is negligible. Fast (6) has also noted that silicon transfers less readily at the higher bulb temperatures.

Spectrographic analysis of the titanium used in determination of the mechanical and working properties of the metal (as discussed later) showed the presence of traces of copper, magnesium, and calcium. The only additional impurities other than the tungsten contributed by the core (0.05 per cent) were silicon (estimated at 0.01 to 0.05 per cent) and in the case of the material produced at 175°C. iron (estimated at 0.01 to 0.1 per cent). Titanium analysis showed that the total impurities were less than 0.2

per cent and probably less than 0.1 per cent. Inherent limitations in the analysis prevent more accurate evaluation. The crude titanium used in preparing this metal was commercial lump titanium obtained from the Titanium Alloy Manufacturing Company and analyzed about 98.6 titanium. Oxygen, carbon, and nitrogen were the chief impurities, the only transferable impurities present in measurable quantities being silicon and iron.

The filament temperature exerts a pronounced effect on the deposition rate, and, in most cases, deposition rates are maintained well below the maximum attainable in order to assure that the filament does not burn out. At high filament temperatues, the deposit tends to be relatively smooth, whereas at lower temperatures well-developed crystal faces may be obtained.

The bars produced are remarkably uniform in cross-sectional area if provision is made for uniform distribution of iodide vapor throughout the bulb. However, if deposition becomes too rapid, the reaction may not be able to proceed uniformly and, as the resistance is lowered at constant voltage, the temperature of the wire may become sufficiently high in certain zones to fuse the filament.

The other factor tending to produce burnouts at the lower bulb temperatures is the reaction of titanium with the tetraiodide. If the filament temperature is set too low during adjustment of the filament current, cutting of the filament by the tetraiodide will take place. If all changes are gradual, however, neither of the above problems are encountered; but they do become important when rapid deposition is desired.

The deposition rates vary to a pronounced degree with the filament temperature, the concentration of iodide vapor, and the reactivity of the crude metal with the liberated iodine. At present, 24-inch hairpins, approximately 300 g. in weight are obtained at a bulb temperature of 175°C. in approximately 30 hours, but the operating time is governed largely by a desire to avoid the necessity for constant attention by using a lower deposition rate. The operating time can be cut to 20 hours with the above equipment and procedure, if optimum filament temperatures are maintained throughout the run.

MECHANICAL AND WORKING PROPERTIES

No report of mechanical properties of iodide titanium has been made in the technical literature with the exception of a few hardness determinations. It has been of interest, therefore, to determine tensile properties, as well as hardness on rod and strip of iodide titanium, and to determine the change in these properties with cold work.

Hardness

The hardness of iodide titanium as deposited cannot be established definitely because of the marked effect of conditions of deposition, particularly the presence of varying amounts of impurities in the crude metal charge. With stabilized operating conditions, in fact, hardness determinations become a convenient indication of the purity of deposit.

Hardness values as obtained by J. H. de Boer (7) were 122 and 188 Vickers[2] (5 kg.) on two specimens. In current production the hardness of

[2] For practical purposes the numerical values for Vickers and Brinell hardness may be taken as the same in the range of hardnesses found for titanium.

titanium rods as deposited has been consistently about 90 Vickers (10 kg.), although values as low as 60 and as high as 135 have been obtained in a few runs. This may be compared to a hardness of 225–250 Vickers for

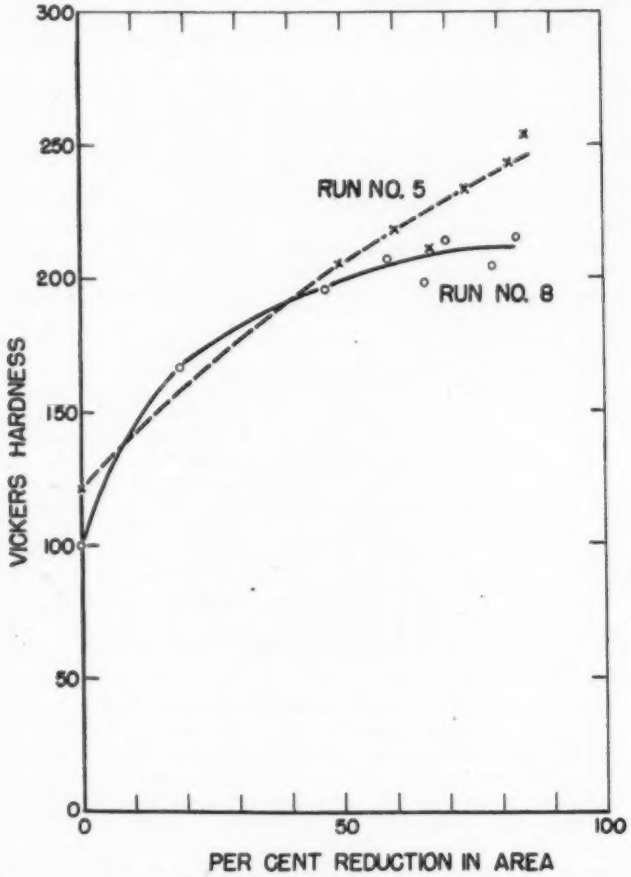

FIG. 5. Increase in Vickers hardness (10 kg.) on cold swaging as-deposited rods from approximately $\frac{1}{4}$ in. (8.5 mm.) to $\frac{1}{8}$ in. (3.2 mm.) diameter.

annealed ductile titanium made from sintered titanium powder produced by the Kroll or Bureau of Mines process.

The effect of cold work on hardness when swaging two rods in the as-deposited condition from a diameter of 0.3–0.34 in. (7.6–8.6 mm.) to $\frac{1}{8}$ in. (3.2 mm.) diameter is illustrated in Fig. 5. Both lots of titanium were somewhat harder initially than normal. The softer one, Run No. 8, in-

creased in hardness only to 210 Vickers (10 kg.) on cold swaging to an 83 per cent reduction in area, and the hardness remained relatively constant after a 50 per cent reduction in area; the harder rod work hardened to a markedly greater extent.

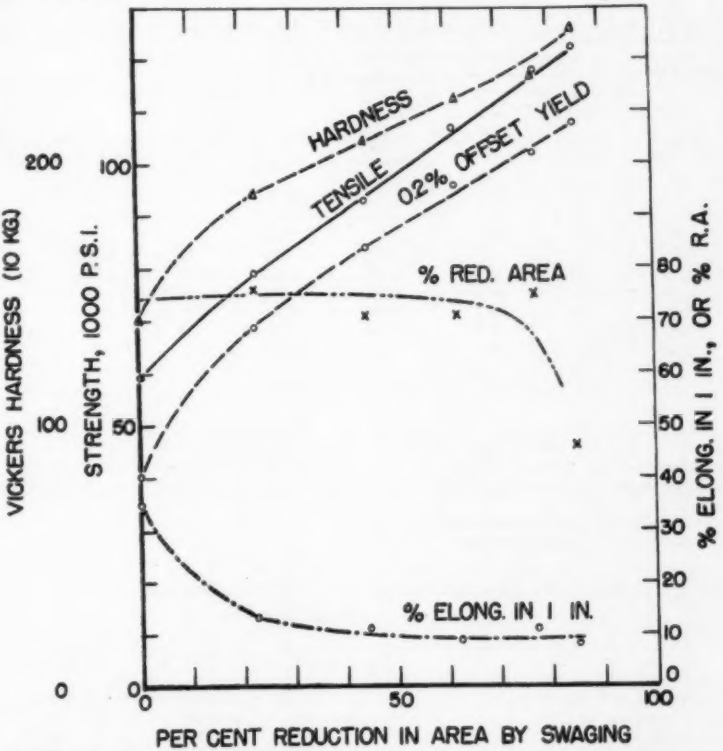

FIG. 6. Tensile properties of $\frac{1}{8}$ in. cold-swaged rods with variable amounts of cold reduction.

Tensile Properties

Specimens of $\frac{1}{8}$ in. (3.2 mm.) rods which had been cold worked to variable extents, up to 85 per cent reduction in area, were prepared for tensile tests by taking samples of the rod from Run No. 5 at convenient intervals during swaging, annealing for 1 hr. at 850°C. in high vacuum (0.05 micron or better), and cold swaging the rest of the way to $\frac{1}{8}$ in. (3.2 mm.). Vacuum annealing of a specimen was carried out by suspending the rod by a fine molybdenum wire in an evacuated pyrex bulb and bringing to temperature in an induction furnace. Temperature was measured with an optical pyrometer, making use of the emissivity values of Went (8).

Results of tensile tests on these cold-worked rods are plotted in Fig. 6.

Numerical data and details of testing are given in Table I. Also given in Table I are the results of a tensile test on $\frac{1}{8}$ inch (3.2 mm.) rod from Run No. 8, cold swaged to 83 per cent reduction from the as-deposited condition. It is seen that the tensile strength of the Run No 5 material increases al-

TABLE I. *Tensile properties of $\frac{1}{8}$ inch (3.2 mm.) swaged iodide titanium rod*

Annealing condition: 1 hour at 850°C. in vacuum

Cold swaging			Tensile Tests*				
Original diameter	Final diameter	Reduction by swaging	Ultimate tensile strength	0.2% offset yield strength	Elongation in 1 Inch	Reduction in area	Hardness, Vickers (10 kg.)
Rod from Run No. 5							
in.	*in.*	*% R.A.*	*psi.*	*psi.*	*%*	*%*	
0.124	0.124	0†	59,500	41,000	35	75	140
0.138	0.122	22.5	79,400	69,000	13	75	189
0.168	0.125	44.5	93,000	84,000	11	70	209
0.198	0.123	62	107,000	96,000	9	70	225
0.265	0.124	77.5	118,000	102,000	11	75	235
0.34‡	0.133	85	122,000	108,000	8	45	252
Rod from Run No. 8							
0.30‡	0.122	83	105,000	94,000	10	70	215

* Test carried out on single specimens for each condition on a Baldwin-Southwark machine, 2000-lb. range, using flat grips. O. S. Peters recording extensometer was of clamp-on type having a gage length of $\frac{3}{4}$ in. (19 mm.).

† Recrystallized grain size about 0.020 mm.

‡ Swaged from as-deposited metal.

TABLE II. *Mechanical properties of rolled iodide titanium strip*

Thickness—0.028 inch (0.7 mm.)

	Cold rolled*	Annealed†
Proportional limit, p.s.i.	49,200	49,500
0.1% Offset yield, p.s.i.	92,000	49,500
0.2% Offset yield, p.s.i.	104,000	49,500
Ultimate strength, p.s.i.	127,500	59,500
Elongation, % in 2 in.	5	37
Modulus of elasticity, p.s.i.	13,100,000	14,100,000
Vickers hardness (10 kg.)	268	158

* Cold rolled to 0.028 x 0.75 in. strip from .300 in. as-swaged rod.

† Annealed in vacuum 1 hr. at approximately 600°C. Recrystallized grain size about 0.005 mm.

most linearly from 60,000 p.s.i. in the annealed condition to 122,000 p.s.i. in the condition of cold swaging to 85 per cent reduction. The Run No. 8 metal, originally slightly softer than that from Run No. 5, increased in strength only up to 105,000 p.s.i., in accordance with its lower final hardness. The specimens necked down to a considerable extent as is shown by the high reductions in area. The elongation leveled off at about 10 per cent in 1 in. from 40–85 per cent cold reduction. The ratio of the 0.2

per cent offset yield strength to the ultimate tensile strength, 0.87–0.90, found for cold-worked iodide titanium is not an uncommon one for most metals and alloys in the cold-worked condition. The yield in the test on

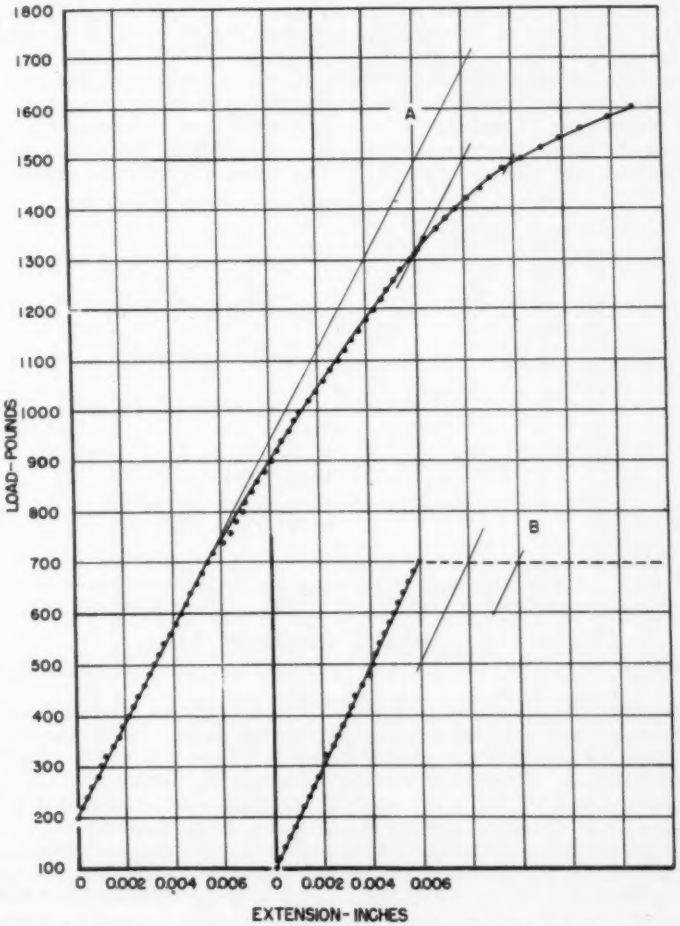

FIG. 7. Load-extension curves of rolled iodide titanium strip. A, cold rolled; B, annealed.

the annealed specimen took place at a fixed load, in a manner analogous to the yield in annealed low-carbon steel, although no upper and lower yields were observed. This indicates that yielding takes place as a block movement of the crystals, such as is found in twinning mechanisms.

A strip of iodide titanium, 0.028 x 0.75 in. (0.7 x 19 mm.), was prepared from 0.3 in. (7.6-mm.) swaged rod from Run No. 5 by a combination of straight and cross rolling. The rod was straight rolled to 0.25 in. (6.35 mm.), cross rolled to 0.105 in. (2.7 mm.), and straight rolled to 0.028 in. (0.7 mm.) without intermediate annealing, a cold reduction of 77 per cent in area. One part of the strip was annealed in high vacuum for one hour at barely a red heat (roughly 600°C.).

Standard 2 inch gage length tensile coupons were machined from the annealed and cold-rolled specimens, and tested for the customary mechanical properties. Stress-strain characteristics were determined using a clip-on dial gage extensometer calibrated in 0.0001 in. divisions. Results of the tests are given in Table II. The stress-strain curves obtained on

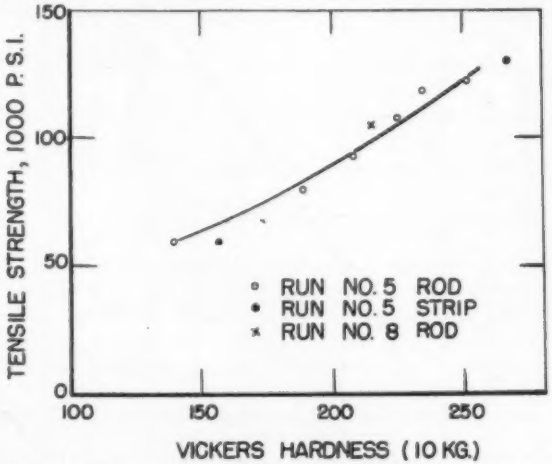

FIG. 8. Relation of tensile strength to Vickers hardness of iodide titanium

these specimens are shown in Fig. 7. The strength and ductility figures check rather well with the values found for the swaged rod specimens, except that the yield for the annealed strip specimen was higher than that found for the rod specimen. It was noted during testing that the yield at constant load for the annealed strip specimen was accompanied by the appearance of a series of parallel markings on the surface of the specimen which later disappeared as the load increased to the ultimate. These most probably were deformation twins because audible clicks could be heard during their formation. Twinning, being a block movement of metal, frequently occurs with the emitting of audible clicks. During a hardness test on annealed material, a crunching noise, evidence of the same phenomenon, is heard. Also, when as-deposited iodide titanium rods are bent, a sound similar to "tin cry" is heard; this is a result of the formation of these deformation twins.

Plotting of the strength-hardness data found for the various tensile tests permits a correlation between Vickers hardness and ultimate tensile strength to be made (Fig. 8).

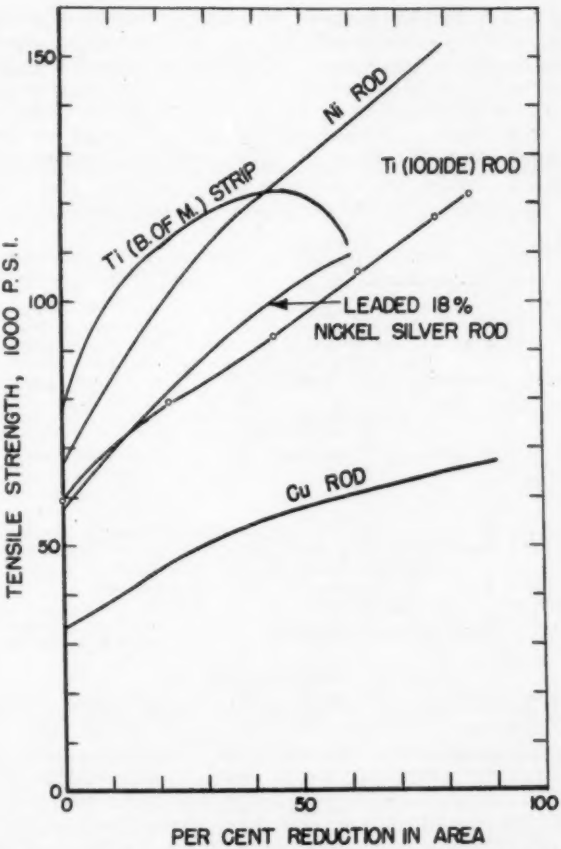

FIG. 9. Comparison of work-strengthening characteristics of iodide titanium with other materials.

It is of interest to compare the work-strengthening characteristics of iodide titanium with the magnesium-reduced titanium reported by the Bureau of Mines and with some other metals and alloys[3], as is shown in

[3] Data taken from the following sources:
a. Copper: ½ in. O.F.H.C. rod annealed 2 hr. at 500°C. and cold drawn. S. Rolle and H. M. Schleicher, Metals & Alloys, **11**, 82 (1940).
b. Nickel: "A" nickel rods, cold drawn, W. A. Mudge, Metals Handbook, ASM, 1939, p. 1664.
c. Bureau of Mines Titanium: $\frac{1}{16}$ inch strip, cold rolled. R. S. Dean, J. R. Long, F. S. Wartman, and E. T. Hayes, Trans. AIME, **166**, 388 (1946).
d. Leaded 18 per cent Nickel Silver: 18 Ni-19 Zn-1 Pb-62 Cu rod, cold drawn. T. C. Merriman, Metals Handbook, ASM, 1939, p. 1448.

Fig. 9. It is seen that the magnesium-reduced titanium strip produced by the Bureau of Mines initially is 20,000 p.s.i. stronger than iodide titanium, work strengthens at a higher rate to about the same peak strength and becomes overworked at 40–50 per cent reduction. Iodide titanium, on the other hand, does not show any evidence of becoming overworked, and, presumably, could be cold worked indefinitely but would not increase in strength much over 130,000 p.s.i. The position of iodide titanium in

TABLE III. *Physical properties of iodide titanium*

Quantity	Unit	Temperature, °C.	Value	Reference
Atomic number			22	Int. Union of Chem. 1935
Atomic weight			47.90	Int. Union of Chem. 1935
Density	g./cm.^{3}	20	4.507	Fast, Z. anorg. u. allgem. Chem., **241**, 42 (1939)
Crystal structure	Angstroms	Room	H.C.P. a 2.953 c 4.729 c/a 1.601	G. Hagg, Z. phys. Chem., **11**, 433 (1930)
	Angstroms	Above 880	B.C.C. a 332	Burgers and Jacobs, Z. Krist. **94**, 299 (1936)
Melting point	°C.		1725 ±10	de Boer, private communication to van Arkel
Boiling point	°C.		above 3000	Handbook, Chemistry and Physics
Resistivity	ohm–cm.	20	42×10^{-6}	Fast, Z. anorg. u. allgem. Chem., **24**, 42 (1939)
Temperature coefficient of resistivity	°C.$^{-1}$	not given	5.46×10^{-3}	Fast, *ibid.*
Mean specific heat	cal./g.	0–219 0–266 0–320 0–500	0.1291 0.1316 0.1334 0.1386	Jaeger, *et al.*, Proc. Acad. Sci. Amsterdam, **39**, 442, 453, 462 (1936)
Mean linear coefficient of thermal expansion	°C.$^{-1}$	20–300	8.2×10^{-6}	Fast, Z. anorg. u. allgem. Chem., **241**, 42 (1939)
Spectral emissivity	(wave length) (6500 Angstroms)	1150°K. 1250°K. 1350°K. 1450°K. 1550°K. 1650°K.	0.533 0.523 0.502 0.480 0.450 0.419	J. Went, in private communication to van Arkel, "Reine Metalle," 1939

work-strengthening characteristics appears to be between nickel and copper and is rather similar to 18 per cent nickel silver.

Because of its high capacity for cold work, there is little need for hot working iodide titanium, particularly in view of the danger of contaminating it with dissolved oxygen and nitrogen in the process. However, if suitable precautions are taken against atmospheric attack, the metal can, of course, be hot rolled with ease. Despite its ductility, iodide titanium exhibits the well-known seizing tendency of titanium and zirconium, and, judging from work done so far, it cannot be cold drawn or deep drawn without providing the necessary lubricating or antiseizing surface, as by controlled oxidation, electroplating, or the like.

An investigation has not been made of the electrical and other physical

properties of the iodide titanium produced in current work. However, rather reliable information is available on such properties of titanium produced largely by the Philips Company in Holland. These are listed in Table III.

ACKNOWLEDGMENT

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Any discussion of this paper will appear in the discussion section of Volume 93 of the Transactions of this Society.

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THE DISSOLUTION OF ALUMINUM IN SODIUM HYDROXIDE SOLUTIONS[1]

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ABSTRACT

The effect of immersion time, temperature, concentration, and an applied external current on the dissolution of commercially pure aluminum in sodium hydroxide solutions is described. A technique resulting in reproducible dissolution rates is given. The instantaneous rate of dissolution increases at a decreasing rate with immersion-time and is directly proportional to the weight-loss and inversely proportional to the immersion-time. The effect of temperature on the rate of dissolution is given by the Arrhenius equation. It is shown that the changing rate and electrode potential are determined by the precipitate which forms local cathodes on the surface of the metal during dissolution. The electrode potential varies as the rate of dissolution, a measure of the local cell current, varies.

When aluminum is made cathodic in sodium hydroxide solutions, the rate of dissolution is decreased only slightly. Making aluminum anodic in sodium hydroxide solutions gradually eliminates hydrogen evolution at the anode as the current density is increased until it is stopped entirely (local cell action is suppressed), and the weight-loss is electrochemically equivalent to the external current. This decrease in local cell action (nor-

[1] Manuscript received March 1, 1948. This paper, based upon a thesis presented to the faculty of the Graduate School of Lehigh University, Bethlehem, Pa., by the author in partial fulfillment of the requirements for the degree of Doctor of Philosophy, prepared for delivery before the Columbus, Ohio Meeting, April 14 to 17, 1948.

mal dissolution) is directly proportional to the anodic current density and is reproducible.

It is found that the various phenomena accompanying the dissolution of aluminum in sodium hydroxide solutions, as described in this paper, may be explained in terms of electrochemical theory.

I. THE EFFECT OF IMMERSION-TIME, TEMPERATURE, AND CONCENTRATION OF SODIUM HYDROXIDE

Introduction

The mechanism of the dissolution of aluminum in various aqueous solutions has been studied by a number of investigators, but final proof of an electrochemical mechanism has been given only in the case of neutral alkali chloride solutions by Brown and Mears (1). In the case of acid and alkaline solutions there are indications that the mechanism is also electrochemical; however, the experimental evidence is often contradictory (2). It is the purpose of the present study to investigate further the mechanism of the dissolution of aluminum in sodium hydroxide solutions.

It has been repeatedly observed that the rate of dissolution of aluminum in acids may be increased several fold by the addition of other metals to the system as alloying elements (3, 4, 5, 6), in powdered form rubbed on the surface of the metal (7), or in the electrolyte in the form of salts (4, 8, 9, 10).[2] Such metals (Pt, Fe, Cu, Ni, Au, Zn, and Hg), when added in the form of salts, are observed to deposit on the dissolving aluminum by chemical replacement (cementation). This accelerating effect, first observed by A. de la Rive (11), is usually considered an indication of an electrochemical mechanism of dissolution.

Even though the accelerating effects of some impurities on the rate of dissolution of aluminum have been known for some time, the effects of these variables on the rate of dissolution in alkaline electrolytes were not definitely determined and recognized until 1939. Isgarischew and Jordansky in 1927 (3) and also Maass and Wiederholt in 1929 (13) found that increasing amounts of copper alloyed with aluminum accelerate its dissolution in both hydrochloric acid and potassium hydroxide. Without taking note of these results, Centnerszwer (5) and Schikorr (14, 15) found that the rate of dissolution of aluminum in sodium hydroxide is independent of the purity of the metal. These investigators, however, used too small a volume of dilute solutions and aluminum of insufficient purity to permit conclusions on the effects of these variables.[3] Not until 1938–39 did Müller (16) and Straumanis (17) prove again that the rate of dissolution of aluminum in alkaline solutions is accelerated by impurities in the metal or in the electrolyte. Further evidence indicating an electrochemical mechanism for the dissolution in alkaline solutions is given by the appearance of the "difference

[2] When impurities are added to the electrolyte in the form of salts, not only the action of the cation but also that of the anion must be considered (3, 12). This fact has sometimes been disregarded (4).

[3] The accelerating effect of impurities falls off rapidly as their concentration is increased. Only 0.01 per cent of iron or copper produces a definite increase in the rate of dissolution. When the iron content is increased fifty times, the rate of dissolution is increased only two or three times (17).

effect" when aluminum is made anodic by an external current. This phenomenon is considered in Section III.

Previous work on dissolution rates of aluminum has not resulted in reproducible rates. The data on the "difference effect," based on the assumption that the dissolution rate of aluminum in sodium hydroxide solutions is constant with immersion-time, have also not been reproducible. The first part of the present study, therefore, includes the development of an experimental technique leading to reproducible dissolution rates and the effect of immersion-time, temperature, and concentration on these rates.

Experimental

Materials

The aluminum used for all experiments was taken from a sheet of 2S-O (about 99.1 per cent)[4] aluminum, 0.0225 inch thick. Fig. 1 gives the di-

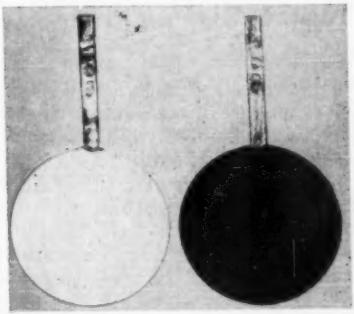

FIG. 1. Specimen with coated handle used for all dissolution runs. Dimensions: radius of disc, 1 in., handle $1\frac{5}{8}$ x $\frac{3}{16}$ in., original thickness 0.0225 in. At left, appearance before a run. At right, specimen covered with precipitate after 60 min. immersion in 0.30N solution at 23°C.

mensions of the specimens used for all runs. A circular design was chosen to minimize edge effects. The electrode was punched in one piece by means of a steel die, thus avoiding a metal-to-metal junction between the disc and the handle. The handle was made $1\frac{5}{8}$ inches long, permitting immersion of the top of the electrode disc $1\frac{1}{4}$ inches below the surface of the solution. On removal from the steel die, the electrodes were filed at the edges and rubbed with emery paper to eliminate burrs. The discs were then flattened by a pressing operation. The electrodes now weighed about 3.7 g. To relieve stresses caused by cold working during punching and filing, the electrodes were annealed at 360°C. in an electric furnace for thirty minutes at temperature and were then allowed to cool in the furnace.

In order to prepare the aluminum surfaces chemically, the electrodes were immersed in sodium hydroxide solutions of about the same concentration as the solution in which they were to be used until the surfaces were uniform

[4] The impurities consist primarily of iron and small amounts of copper and silicon.

and all scratches had been eliminated. During the dissolution process, a black precipitate (Fig. 1) gradually forms which can be removed only by wiping the surface under running water. A stream of water alone does not wash off the precipitate. About 0.4 g. of aluminum is lost during this chemical preparation, and the thickness is reduced about 0.0025 inch. The diameter of the specimen does not change appreciably during this process nor during subsequent dissolution tests.

The concentration of sodium hydroxide was controlled by titration with standard hydrochloric acid solution using phenolphthalein indicator. Reagent grade sodium hydroxide was used. Initial concentrations were within ± 0.004N of the given normality. The concentration of sodium hydroxide in effect remained constant throughout a run because of the large volume (4 liters) of solution used (100 ml. solution per cm.^{2} of aluminum surface). No changes in the acid titration or dissolution rates were detected when 10 per cent of the equivalents of the sodium hydroxide in the solution was used up as calculated by the weight of the aluminum dissolved. Distilled water was used for all runs.

Specimen coating

The use of the above described specimen depends entirely on an efficient coating for the handle. The part of the handle which is immersed in the solution must be completely protected from access by the electrolyte to insure a constant surface exposed (the disc). Also, when the specimen is used as an electrode in an electrolytic cell, the current density in an unshielded handle would be much greater than over the remainder of the specimen, resulting in rapid dissolution of the handle. Previous investigators have used paraffin-wax and similar coatings for shielding. The poor adherence of these substances often leads to penetration of the solution under the edges of the coatings which also are generally not resistant to alkaline solutions.

After several types of coatings had been tested, a laboratory cement[5] was tried which gave satisfactory performance. This cement is transparent and can be removed quantitatively from the specimens with acetone.

The properties of the laboratory cement of importance to this work are its resistance and protection against concentrated hydroxides and acids (HCl), adherence to aluminum without peeling at edges during exposure to various electrolytes, constancy in weight during a dissolution test making removal for weighings unnecessary, and ability to dry rapidly (10 to 15 minutes).

Reproducibility

In order to obtain reproducible dissolution rates, the initial surface of the aluminum must be uniform in its break-down characteristics throughout all tests. Usually three distinct, successive phases are observed during dissolution (18, 19): first, incubation period during which there is no visible change, i.e., no hydrogen evolution, because of the protection afforded by the oxide film; second, induction period during which there is a sudden initiation of reaction and a rapid increase in hydrogen evolution as a result of gradual film break-down; and third, the reaction period during which

[5] DEKADHESE, made by Technical Specialties Company, Malden, Mass., under license from Decker Laboratories, Inc.

the oxide film has no further effect on the dissolution rate. To eliminate the first and second phases the specimens were immersed in concentrated (6N) sodium hydroxide solution until hydrogen bubbles appeared (10–20 seconds). The specimens were then rapidly withdrawn, rinsed immediately with water, and immersed in the test solution for a run. The weight-loss during this treatment is not more than one milligram. By this method reproducible dissolution rates and electrode potentials were obtained.

The procedure for all runs using specimens prepared as described above was as follows:

1. Immersion in concentrated (6N) sodium hydroxide solution until hydrogen bubbles appear.
2. Rinsing in water and immediate immersion in the test solution.
3. Removal of precipitate under running water by wiping after withdrawal from the test solution.
4. Drying in electric oven at 110°C. and cooling in desiccator.
5. Weighing.

The specimens were then ready for another run. The runs were timed by stopwatch.

Preliminary experiments revealed that the dissolution rates of aluminum in sodium hydroxide are sensitive to small fluctuations in temperature. A thermo-regulated bath was constructed which permitted temperature control to ± 0.05°C. A mercurial thermo-regulator and a mercury relay were used for this control. The bath held five 4-liter beakers which were used simultaneously for dissolution runs.

A large number of runs were repeated to obtain information on the reproducibility of dissolution rates. In general, the per cent maximum deviation from the arithmetic mean value did not exceed three per cent. Only at small weight-losses (at low concentrations of sodium hydroxide, low temperatures or short time of immersion) was this value exceeded by one or two per cent. The difference in weight-loss for repeated runs in the large majority of cases did not exceed 10 mg.

In an effort to determine the cause of the variations within 10 mg., the effects of several other variables were studied. No variation could be found in the dissolution rates of the various specimens nor in the action of various batches of sodium hydroxide pellets. Within the calculated 10 per cent depletion of the sodium hydroxide solution previously mentioned, no difference was found in the action of a fresh solution and one which had already been used for a run. The different surface conditions produced on the specimens by various concentrations of sodium hydroxide did not appreciably affect the dissolution rates. Neither the number of specimens per beaker nor the position (near the surface or at the bottom) affected the rate. Thus, it was not possible to determine the factors which caused the variations in the weight-losses up to 10 mg. in the case of repeated runs.

To determine the effect of agitation on the dissolution rate, a stirrer was placed below the specimen. It was possible to place the specimen at the edge of the vortex produced by rapid stirring. Both sides of the panel were thus exposed to a rapid flow of liquid, which dispersed the evolved hydrogen throughout the beaker. In every case agitation produced some increase in the dissolution rate. The increase varied from five to twenty per cent.

Experimental results

The effect of time of immersion, temperature, and concentration of sodium hydroxide was studied within the following ranges:

Concentration of sodium hydroxide	0.05–0.50N
Temperature	8.0°–40.0°C.
Time of immersion	5–120 min.

Typical weight-loss versus time data at various temperatures are plotted in Fig. 2 and, as indicated, the weight-loss is not directly proportional to

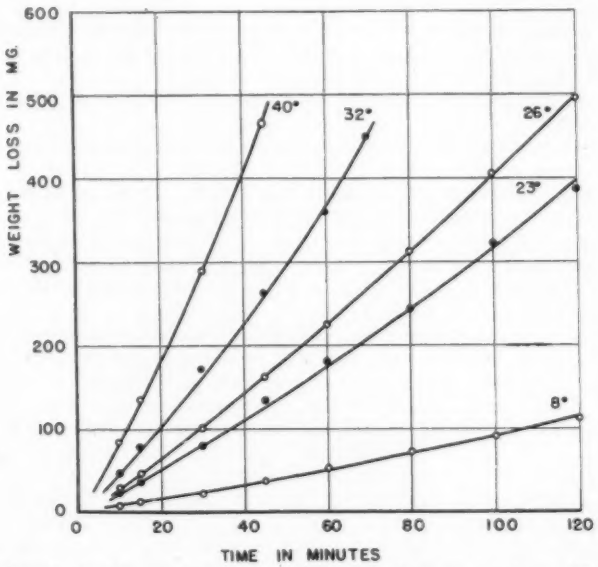

FIG. 2. The effect of immersion-time on the weight-loss per specimen (40.5 cm.²) at various temperatures in 0.20N sodium hydroxide solutions.

the length of time of immersion. The rate of dissolution increases throughout the period of immersion at all temperatures. This was found to be the case at all concentrations studied. The increase in the rate of dissolution is accompanied by a progressive covering of the surface with a black precipitate (Fig. 1). This process continues until only a few pores remain, revealing the metallic surface under the microscope. The surface is then black to the unaided eye. None of this precipitate was found in the solution, nor was there any colorless (aluminum hydroxide) precipitate observed.

The precipitate was collected from a number of specimens and analyzed. The dried precipitate consisted of 51.3 per cent iron and 9.9 per cent copper. A spectrographic analysis indicated that there are also small quantities of aluminum, magnesium, and silicon present. The precipitate is thus formed

chiefly from the impurities in the aluminum. The dissolved aluminum apparently almost entirely enters the solution.

At all concentrations and lengths of times of immersion, an increase in temperature resulted in an increase in the dissolution rate (weight-loss). Increasing concentrations of sodium hydroxide increased the weight-loss in every case. Typical curves of the effect of temperature and concentration are given in Fig. 3 and 4.

Empirical equations were found relating the weight-loss in mg. W per specimen (40.5 cm.^{2}) to the immersion-time t in minutes, the temperature

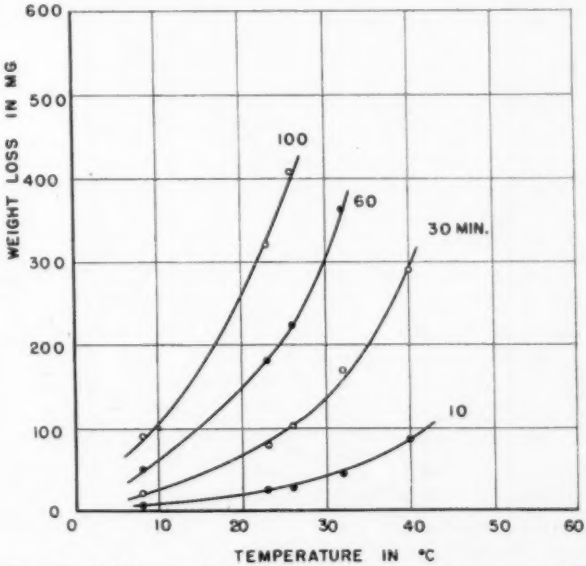

FIG. 3. The effect of temperature on the weight-loss per specimen (40.5 cm.^{2}) for various immersion-times in 0.20N sodium hydroxide solutions.

T in degrees Kelvin, and the concentration C in milli-equivalents per liter. When the weight-loss is plotted against immersion-time on logarithmic coordinates, a straight line results. The effect of immersion-time on weight-loss may, therefore, be represented by a power function,

$$W = at^b \qquad (I)$$

where a and b are constants. These constants were calculated by the method of averages for all conditions studied. Values for a and b are given in Table I. The values of b do not show a consistent trend with changes in T and C. The values of a increase with increasing temperature and concentration and give the weight-loss during the first minute of immersion.

Straight lines are obtained when the weight-loss vs. temperature data are plotted on semi-logarithmic coordinates. The relationship between the

weight-loss and the temperature may thus be given by an exponential function

$$W = me^{nT} \qquad \text{(II)}$$

where e is the base of the natural logarithm and m and n are constants.

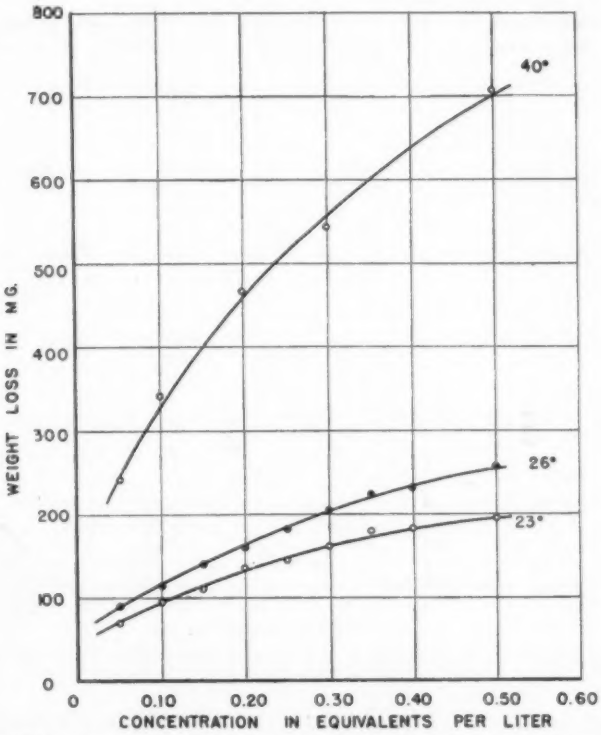

FIG. 4. The effect of concentration of sodium hydroxide on the weight-loss per specimen (40.5 cm.^{2}) at various temperatures for 45 min. dissolution runs.

In Table II, several values for these constants are given which seem to be independent of temperature and concentration.

A plot of the weight-loss vs. concentration data on logarithmic coordinates reveals that the dependence of the weight-loss on the concentration may be given by a power function,

$$W = kC^d \qquad \text{(III)}$$

where k and d are constants. A number of these are given in Table III.

TABLE I. *Constants (a) and (b) for equation* $W = at^b$
W = mg./40.5 cm.²
t = minutes

Temperature	Concentration of NaOH in equivalents per liter				
	0.05	0.10	0.20	0.30	0.50
			(a)		
°C.					
5.0	—	0.530	—	—	—
8.0	—	—	0.658	—	—
8.5	—	—	—	1.060	1.020
23.0	1.175	1.714	1.895	2.660	2.855
26.0	1.378	1.880	2.178	3.220	4.041
32.0	2.210	2.791	3.819	—	—
40.0	3.350	5.017	6.783	9.678	9.860
			(b)		
5.0	—	0.973	—	—	—
8.0	—	—	1.072	—	—
8.5	—	—	—	1.012	1.071
23.0	1.084	1.057	1.113	1.085	1.112
26.0	1.101	1.088	1.134	1.089	1.086
32.0	1.099	1.103	1.116	—	—
40.0	1.117	1.111	1.108	1.070	1.124

TABLE II. *Constants (m) and (n) for equation* $W = me^{nT}$
W = mg./40.5 cm.²
T = absolute temperature in °K.
e = base of natural logarithm

Time of immersion	Concentration of sodium hydroxide solution in equivalents per liter				
	0.05	0.10	0.20	0.30	0.50
			(m)		
min.					
15	113×10^{-9}	15.3	—	23.6	11.9
45	27.5	3.47	6.07	14.6	9.9
120	—	7.19	—	12.7	23.2
			(n)		
15	0.0647	0.0722	—	0.0725	0.0754
45	0.0732	0.0809	0.0802	0.0780	0.0800
120	—	0.0822	—	0.0822	0.0809

The constant k varies with temperature and immersion-time, while d appears to be independent of these variables. This is analogous to equation (I).

Agreement of weight-losses calculated with these equations and observed

values was well within experimental accuracy. The differences in these values were below three per cent.

TABLE III. *Constants (k) and (d) in equation* $W = kC^d$

W = weight loss in mg./40.5 cm.^{2}

C = concentration of sodium hydroxide in milli-equivalents per liter

Time of immersion	Temperature in °C.			
	23	26	32	40
		(*k*)		
min.				
15	3.90	6.01	—	10.77
30	7.76	7.47	—	23.66
45	9.64	12.27	23.1	38.94
60	12.79	15.84	—	—
80	24.44	25.79	—	—
100	25.74	33.27	—	—
120	38.59	40.42	—	—
		(*d*)		
15	0.440	0.396	—	0.482
30	0.447	0.496	—	0.477
45	0.491	0.491	0.460	0.468
60	0.499	0.474	—	—
80	0.438	0.469	—	—
100	0.475	0.473	—	—
120	0.440	0.471	—	—

Discussion

The effect of length of time of immersion

By differentiating equation (I) and substituting for a we get

$$\frac{dW}{dt} = \frac{W}{t} b. \qquad \text{(IV)}$$

Thus, the instantaneous rate is directly proportional to the average rate throughout the ranges of temperature and concentration studied. The constant of proportionality b is independent of the temperature and concentration of the solution. An average value for b is 1.11. The rate of dissolution varies directly with the weight-loss and inversely with the immersion time. The effectiveness of the impurities in each milligram of aluminum dissolved in increasing the rate of dissolution decreases with the immersion-time until, finally, further dissolution does not affect the rate which then remains constant. In Fig. 5 are plotted weight-loss data up to 360 minutes immersion-time. It is seen that in 0.30N solution at 23°C. the rate becomes constant at about 160 minutes.[6] Therefore, the rate of dissolution increases at a decreasing rate approaching a constant rate in

[6] During these runs no solution was used longer than 180 minutes. After this period the specimens were rapidly removed to a new solution.

the ranges studied. All equations apply to this range, i.e., before a constant rate is reached during the reaction period since the incubation and induction periods are eliminated by the pre-treatment.

Tammann and Neubert (6) have derived an equation for the effect on the

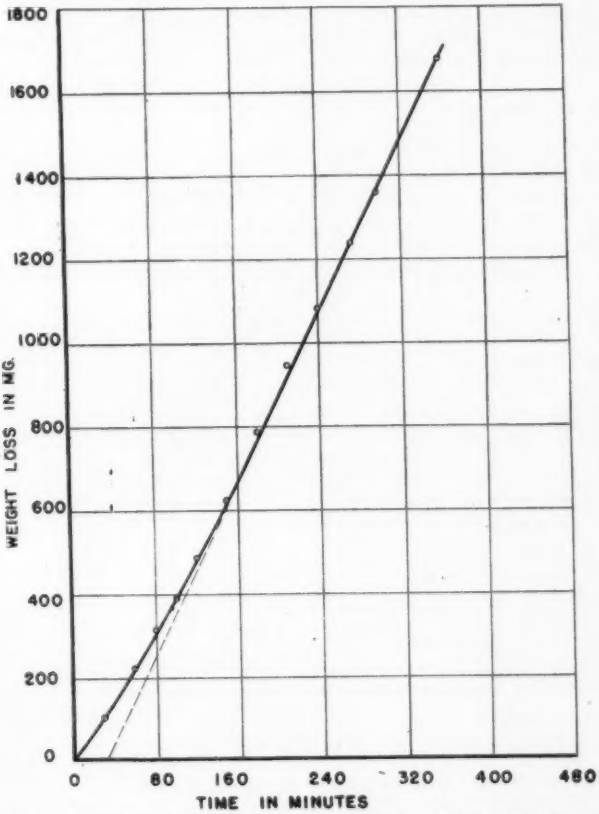

FIG. 5. The effect of immersion-time up to 360 min. on the weight-loss per specimen (40.5 cm.²) in 0.30*N* sodium hydroxide at 23°C. Note that rate of dissolution becomes constant after about 160 min. of immersion.

rate of dissolution of impurities in the metal which, on dissolving, precipitate on the surface in the metallic state or as compounds,

$$\frac{dW}{dt} = k' + k''t. \qquad \text{(V)}$$

Evans (25) has suggested a modification of this equation,

$$\frac{dW}{dt} = k' + k''W. \qquad \text{(Va)}$$

This equation holds only as long as the impurities adhere to the surface. Tammann agrees that (Va) is the equation to be expected, as W is a measure of the impurities available for precipitation on the surface. Integration of (Va) gives an equation for W for which a plot of W vs. t on semilogarithmic coordinates is a straight line. The data obtained in this study do not

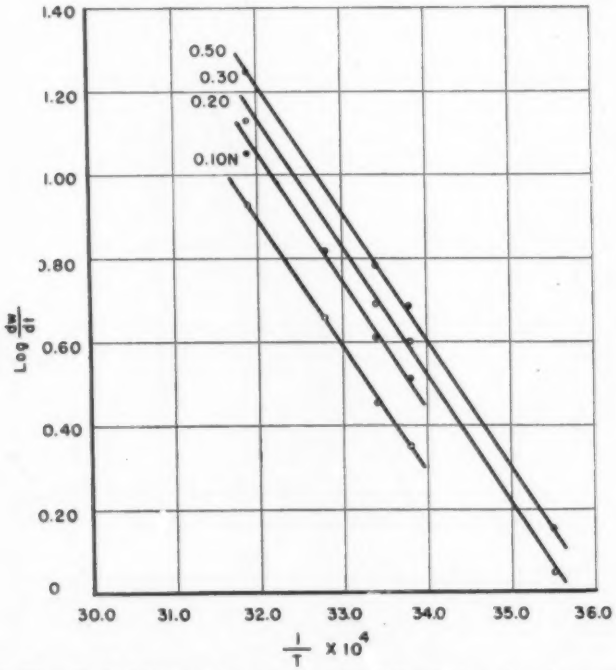

FIG. 6. The effect of temperature on the rate of dissolution at various concentrations of sodium hydroxide. All runs 45 min.

give straight lines on these coordinates; logarithmic plots are required to give straight lines. Equation (Va), therefore, does not apply to any part of the dissolution process studied. It will be shown in the section on electrode potential behavior that these equations do not apply in this case because they do not provide for the effect of polarization.

The effect of temperature

A plot of the logarithm of the instantaneous rate of dissolution against the reciprocal of the absolute temperature gives straight lines at various

concentrations (Fig. 6) and immersion-times. The effect of temperature on the instantaneous dissolution rate may thus be given by the Arrhenius equation (21),

$$ln \frac{dw}{dt} = lnA - \frac{E}{RT}$$

or

$$\frac{dw}{dt} = Ae^{-E/RT} \qquad \text{(VI)}$$

where R is the gas constant, E is the difference in the heat content between the activated and the inert molecules, the "experimental energy of activation," and A is a constant which is independent of the temperature. This relationship represents the temperature dependence of the specific reaction rates of most chemical reactions. Equation (VI) is widely applicable not only to homogeneous reactions but also to heterogeneous processes (22, 23).

The "experimental energy of activation" of the rate-controlling process in the dissolution of aluminum in sodium hydroxide was found to be about 13,700 cal. per mole for various concentrations and immersion-times.[7]

The rate of dissolution approximately doubles with an increase of 10°C. for all concentrations of sodium hydroxide and various immersion-times.[8] This is generally considered to be true for homogeneous chemical reactions (23). In contrast, for those *heterogeneous* reactions whose rate is determined by a diffusion process, the increase in reaction rate for a 10° rise is expected to be of the same order as the change in the diffusion constant, i.e., 2–3 per cent (24).

The effect of concentration

It was not possible to relate the rate of dissolution over the entire range of concentration of sodium hydroxide to any one property of the solution.[9] Neither the weight-loss nor the rate of dissolution is directly proportional to the pH, the conductivity, or the normality of the solution. The weight-loss was found to be directly proportional to the hydroxyl ion concentration up to 0.30N. Between 0.10N and 0.50N the rate of dissolution is proportional to the square root of the hydroxyl ion concentration as calculated from pH measurements.

II. ELECTRODE POTENTIAL BEHAVIOR

Experimental

A diagram of the experimental arrangement used for all electrochemical studies is given in Fig. 7. During measurements of open-circuit electrode potentials the bridge connecting the two reaction beakers was removed and

[7] The slope of the lines in Fig. 6 is $\frac{-E}{R \times 2.3}$, where R is given in calories per degree (1.98).

[8] Typical coefficients are 1.92 and 2.15.

[9] It is shown in the section on "Electrode Potential Behavior" that the slope of the self-polarization curve is directly proportional to the pH of the solution.

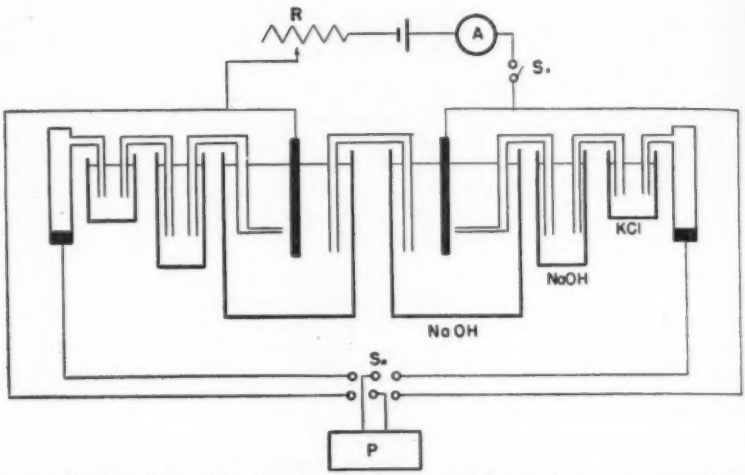

FIG. 7. Experimental arrangement used for electrode potential measurements and the application of an external current.

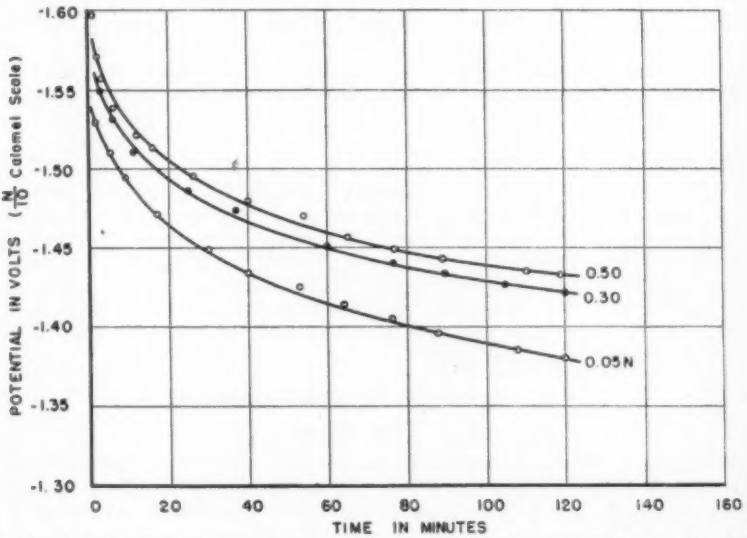

FIG. 8. The effect of concentration of sodium hydroxide on the electrode potential of dissolving aluminum at 23°C.

the switch S_1 was open. It was then possible to obtain two potential vs. time curves during one run by connecting the potentiometer to each of the

two independent circuits through the double-pole double-throw switch. The sodium hydroxide in the bridges and intermediary solutions was of the same concentration as that in the reaction beaker. The bridge connecting the reaction beaker with the other parts of the system was bent as indicated and drawn to a capillary opening which was brought as close to the surface of the aluminum specimen as possible. The tubulus could not be pressed against the surface because hydrogen bubbles fill the capillary when it is brought too close to the surface.

The calomel cells contained tenth-normal potassium chloride saturated with calomel. The potentiometer readings were made to 0.01 millivolt. The beakers containing solutions and the calomel cells were immersed in

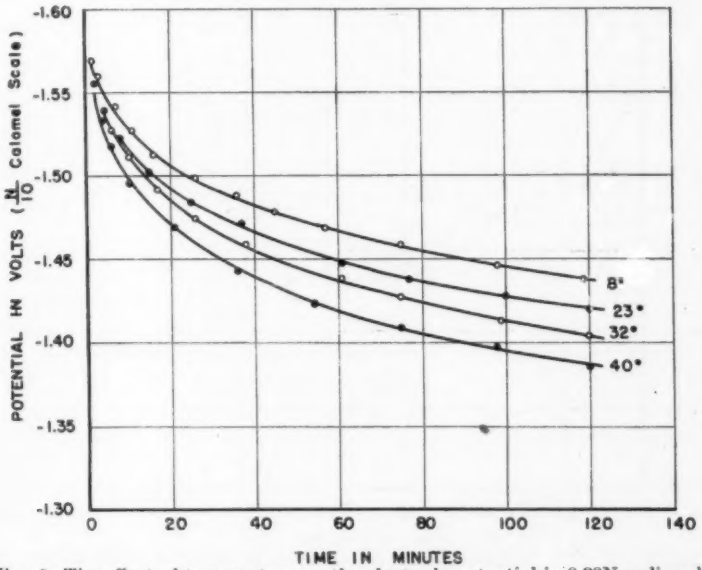

FIG. 9. The effect of temperature on the electrode potential in 0.30N sodium hydroxide solutions.

the constant-temperature bath. All runs were made at 23°C. except one series which was made to determine the effect of temperature. The temperature coefficient of the calomel cell was neglected in these measurements. The concentration of sodium hydroxide used was 0.30N except in one series of runs which was made to determine the effect of concentration on the electrode potential. Junction potentials were computed by Henderson's equation (23). When these corrections are applied to the measured potentials, the sequence of the curves in Fig. 8 is not changed. Since changes in electrode potential rather than absolute values are of primary importance in this study, the corrections for junction potentials were not applied to the data.

Results

For all electrode potential measurements the specimens were pre-treated as described for dissolution tests. Immediately on immersion in the reacting solution, measurements were made timed with a stopwatch. The electrode potential vs. time curves thus obtained were resproducible in every case. This reproducibility is primarily an indication of the reproducibility of the pre-treatment and the formation of the precipitate. When no pre-treatment is used, the potential behavior is different and not reproducible.

In Fig. 8 and 9 are given the effects of temperature and concentration on the electrode potential behavior of dissolving aluminum. There is a

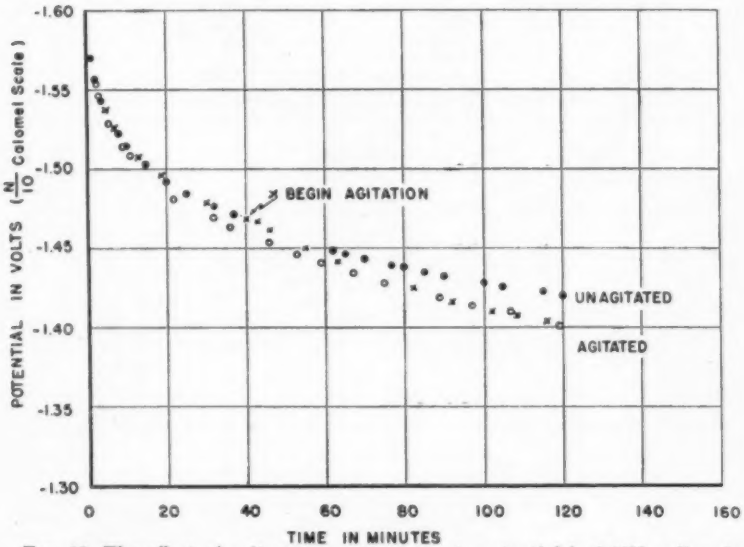

FIG. 10. The effect of agitation on the electrode potential in 0.30N sodium hydroxide at 23°C.

continuous increase towards more noble electrode potentials in all the curves. Increasing temperature shifts the potential-time curve towards more noble values, while increasing concentration causes a shift towards more negative values. Both of these effects increase the rate of dissolution.

Agitation shifts the electrode potential towards more noble values as shown in Fig. 10. This effect becomes more pronounced with increasing time of immersion. When agitation is begun after sixty minutes' immersion-time, the electrode potential curve shifts to values determined on a specimen exposed to agitation throughout the entire run.

Data obtained to determine the cause of the change in electrode potential

with immersion-time are given in Fig. 11. It is seen that changing to a new solution after 60 minutes has no effect on the electrode potential. Various methods of wiping the surface free of precipitate cause an immediate change to a more negative value of electrode potential. Following such a change there are again regular increases in potential as more precipitate forms.

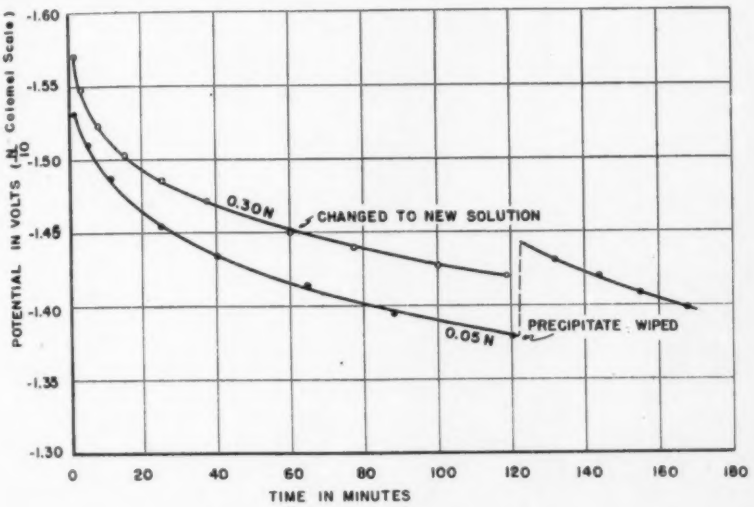

FIG. 11. The effect of wiping precipitate during immersion and changing to fresh solution on the electrode potential at 23°C.

Discussion

The changes in the electrode potential caused by wiping the precipitate from the aluminum sheet during immersion and the absence of a change in the electrode potential when a specimen is removed to a new solution, after a precipitate has formed on the surface, indicate that the electrode potential behavior is largely determined by the action of the precipitate rather than by any changes taking place in the solution during the dissolution process.

There is a continuous change in electrode potential throughout the immersion-time studied. As previously described, there is also a continuous change in the rate of dissolution during the immersion periods studied. When the electrode potential is plotted against the rate of dissolution at a given time of immersion as shown in Fig. 12, straight lines are obtained in every case. Within the ranges of temperature and concentration of hydroxide studied, the electrode potential of dissolving aluminum

is directly proportional to the rate of dissolution.[10] The equations of these lines are of the type

$$E = E' - \frac{dw}{dt} P \qquad \text{(VII)}$$

where E is the measured potential, E' the open-circuit potential, and P, the slope. Rearrangement of (VII) gives

$$\frac{dw}{dt} = \frac{(E' - E)}{P} .$$

The rate of dissolution is directly proportional to the difference between the

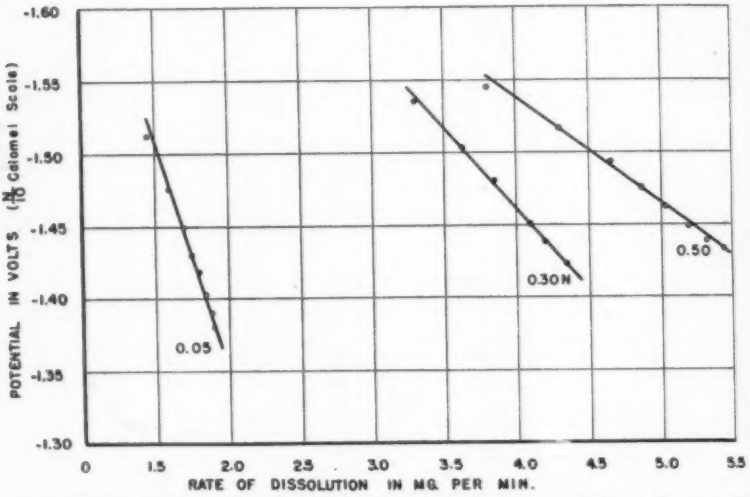

FIG. 12. Correlation of dissolution rate in mg. per specimen and electrode potential at various concentrations of sodium hydroxide at 23°C. Since the dissolution rate is a measure of the local cell current, these lines may be considered as polarization curves.

open-circuit and the measured potential and inversely proportional to the polarizing function.

When equation (VII) is combined with (IV) and solved for W, we get

$$W = \frac{(E' - E)t}{bP} \qquad \text{(VIIa)}$$

The weight-loss is thus dependent not only on the length of time of immersion but also on the polarization conditions. From equations (I, IV, and VII) it can be shown that

$$(E' - E) = abP(t^{(b-1)})$$

[10] This relationship was also found by Straumanis (36, 37) in the case of zinc dissolving in sulfuric acid, and by Hoar and Havenhand (25, 38) for iron.

This is the equation of the potential-time curves. A logarithmic plot of this equation gives a straight line. When the potential-time data are plotted in this manner, straight lines are obtained.

The fact that the rate of dissolution varies as the electrode potential varies indicates that the dissolution process is electrochemical. Therefore, the rate of dissolution may be converted (by means of Faraday's law) to current density.[11] The current density thus obtained is determined by the local-cell current without an external current. We then have a typical polarization curve.

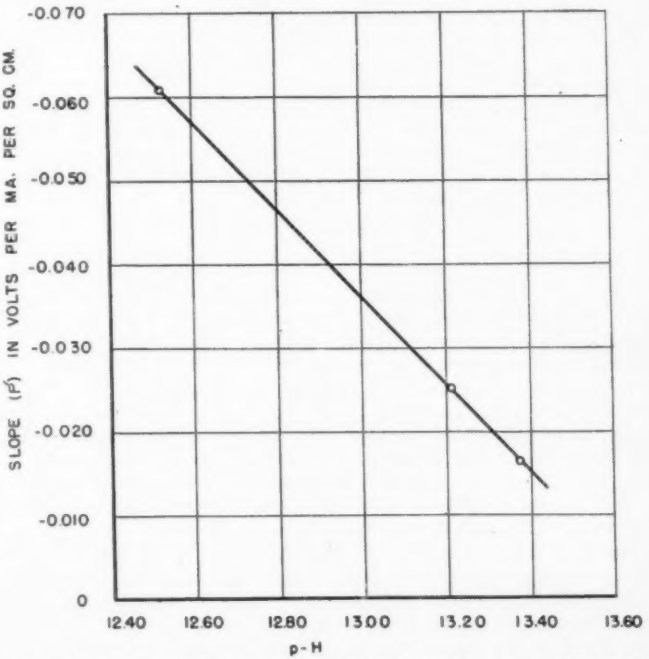

FIG. 13. The effect of pH on the slope of the polarization curve. The rate of dissolution in the slope has been converted to equivalent current density by Faraday's law.

When the polarizing function (slope P′) is plotted against the pH of the hydroxide solution at various concentrations, a straight line results (Fig. 13). The polarizing function is thus directly proportional to the pH of the solution. As the concentration is increased the polarizibility is decreased. According to Fig. 13 (on extrapolation), at a pH of 13.70 it is not possible to polarize aluminum anodically in sodium hydroxide solutions.

These electrode potential and polarization curves may now be interpreted in the light of information gained primarily in acid and neutral

[11] Rate in mg. per 40.5 cm.^{2} × 4.42 = current density in milliamps per cm.^{2} P′ = 4.42P.

solutions (25, 26, 27). It has been found that if, on immersion, the potential of a metal increases with time, it may be inferred that cathodic processes predominate over anodic processes. This increasing potential may be obtained either by an increase in the self-polarization of the anodic areas or by a decrease in the self-polarization at the cathodic areas. In every case, an increase in potential with time has been observed during the dissolution of aluminum in sodium hydroxide solution. It may thus be concluded that cathodic processes predominate.

During dissolution the area of the cathodic phase increases. The slopes of the polarization curves are proportional to the extent of self-polarization and to the anodic area. Since the process is predominantly under cathodic control and the potential varies as the dissolution rate varies, the anode area must remain essentially constant. The higher potential is thus a result of increasing self-polarization of the anodic areas.

The change in the electrode potential brought about by agitation can be accounted for on the basis of the local-cell action just described. The effect of relative motion between electrode and electrolyte is to increase the rate of transfer of reactants and products of reaction between the solution-metal interphase and the bulk solution (27). The result is one or both of the two principal effects at the interphase: cathodic area depolarization, with possible slight anodic area polarization; and/or anodic area depolarization. The direction of the electrode potential change on agitation depends on the relative magnitudes of both. Predominance of the first gives a more positive potential. As indicated in Fig. 10, the potential becomes slightly more positive when the solution is agitated.[12]

The difference in potential, which increases with immersion-time, may thus be attributed primarily to cathodic area depolarization. The mechanism of this depolarizing action, which slightly increases the dissolution rate, probably consists of the removal of hydrogen bubbles from the surface by the action of the flowing solution. In this way, the bubbles are removed while they are relatively small, giving rise to more contact between the solution and the precipitate. This effect increases as the cathodic area (quantity of precipitate) increases.

It was shown in a previous section that the rate of dissolution becomes constant when the immersion-time is extended beyond the period studied (120 minutes). The potential also approaches a constant value. One of the conditions for the steady state as defined by Gatty and Spooner (27) is that there be constant relative areas of all different fields (anodic and cathodic) existing on the solution-electrode interphase. This implies that when a constant potential and rate of dissolution are reached, the cathode area no longer increases.

III. THE EFFECT OF AN EXTERNAL CURRENT

Introduction

When a metal is made an electrode in an aggressive electrolyte, there may be a possibility of suppression of attack by the electrolyte when the specimen is made a cathode. Similarly, the rate of dissolution of the metal may

[12] Gatty and Spooner (27) consider that any electro-kinetic effects, which may be produced by relative motion between the electrode and the solution, are in many cases outweighed by the simultaneous effect produced upon the local action process.

be increased by making it an anode. However, the rate of normal dissolution (rate of dissolution without external current) may be reduced by the external anodic current. This phenomenon is known as the "difference effect."

Several investigators (17, 28) have confirmed Thiel and Eckell's (29, 30, 34) original discovery of a positive "difference effect" when aluminum is dissolved anodically in sodium hydroxide solution. Thiel and Eckell observed that when aluminum dissolving in sodium hydroxide is connected to a more noble metal immersed in the same solution, the hydrogen evolution at the aluminum decreases while hydrogen is also evolved at the more noble metal. Connection of aluminum with a more noble metal actually increases its rate of dissolution even though the rate of hydrogen evolved at the aluminum is decreased.

When aluminum dissolves freely at a given temperature and concentration of electrolyte, it has a certain rate of dissolution, V_H, determined by measuring the hydrogen evolved over a given period. If this same run is now repeated while the aluminum specimen is connected to a more noble metal electrode also immersed in the same solution, the hydrogen evolved over the given period of time from the aluminum alone, V_1, is less than V_H, while the total volume of hydrogen evolved, V_g, is greater than V_H. From the current-time curve obtained from an ammeter connected between the two electrodes, the volume of hydrogen evolved at the more noble electrode, V_e, may be calculated. Then

$$V_g - V_e = V_1 \qquad \text{(VIII)}$$

and

$$V_H - V_1 = \Delta \qquad \text{(IX)}$$

where Δ is defined as the "difference effect." Thiel and Eckell (29, 30) found that, within a certain range of current density, the "difference effect" increases linearly with the current density as measured in the external circuit.

$$\Delta = KI \qquad \text{(X)}$$

In all previous studies of the "difference effect," the assumption was made that the metal dissolves at a constant rate. This is one of the reasons for the non-reproducibility of the effect (20, 28, 29, 30). It has been shown previously in this paper that the rate of dissolution is not constant for commercially pure aluminum dissolving in sodium hydroxide solutions. For this reason, the "difference effect" was studied taking into consideration the change in rate of dissolution with immersion-time.

Results reported by previous investigators on making aluminum cathodic in alkaline solutions are contradictory. Hedges and Myers (31) found that an aluminum electrode connected to a platinum wire in 3N hydroxide solution when made cathodic does not dissolve even though it gives off gas. When the current is reversed, the aluminum dissolves, but the gas does not come from the aluminum. However, Caldwell and Albano (32) found that the rate of dissolution is unaffected (up to a current density of 90 ma. per cm.^{2}) when aluminum is made cathodic in sodium hydroxide solution and that the rate is dependent only on the concentration of the alkali.

Experimental

Two aluminum specimens, one an anode, the other a cathode, were used simultaneously in the experimental arrangement given in Fig. 7. The switch S_1 was closed and the two large reaction beakers, one containing the anode, the other the cathode, were connected by a bridge. The concentration of sodium hydroxide was the same throughout all bridges and beakers for a series of runs. Two series of runs were made, in a 0.30N and in 1.00N solutions. All runs were made at 23°C. and 45 minutes immersion-time. The e.m.f. was supplied by a d.c. generator. Throughout a run the current was held constant (±0.01A) by varying the resistance. As before, the specimens were given a pre-treatment.

Potential measurements were made using the same technique previously described.

For the lower current densities several sodium hydroxide bridges of the same concentration as the solution in the reaction beakers were used to complete the circuit between these beakers. This type of bridge could not be used where higher current densities were desired. The sodium hydroxide bridges were replaced by a platinum wire to increase the current in the circuit. The ends of this wire were placed as far away as possible from the specimens. The error introduced by using a platinum wire bridge (gases were evolved at both ends) was negligible.[13]

The two-beaker arrangement was used because the heat evolved, when the rate of dissolution is increased by an externally applied e.m.f., makes temperature control difficult. Also, by using separate beakers for the anode and the cathode the solutions were not depleted so rapidly as is the case when both are in the same solution.

Results

The results of runs made while an external current was applied to aluminum are given in Fig. 14 and 15. The reproducibility of these runs is of the same order as that of simple dissolution runs previously described. For both the 0.30N and the 1.00N runs the aluminum specimen which was made the cathode lost only slightly less weight than under freely dissolving conditions. After an initial drop of about 10 mg. at a current density of 0.3A, the cathodic weight-loss decreased very slightly with increasing current density.[14] As before, a precipitate formed on the surface.

In 0.30N solution there is no effect on the weight-loss of the anode until a c.d. of 0.3A (per specimen) is reached. At this value the weight-loss becomes proportional to the c.d. up to about 1.1A. From this point on, the slope changes and the proportionality of weight-loss and c.d. continues. When this last section of the curve is extrapolated, it goes through the origin. The changes taking place at the surface as the c.d. is increased are given in a series of photomicrographs in Fig. 16. To the unaided eye the

[13] A check run was made at 0.80A by immersing both anode and cathode in the same beaker (which eliminated the platinum wire connecting the solutions). The weight-loss obtained in this way agreed with that found when the wire was used. The anode-loss with the wire was 225.5 mg.; without the wire, 219.1 mg.

[14] This differs somewhat from the results of Caldwell and Albano (32), who found that making aluminum cathodic in sodium hydroxide solution did not affect the weight-loss. The temperature control used by them was 30.0 ± 0.5°C.

specimens exposed to current densities over 1.2A in 0.30N solution have a polished appearance. However, microscopic examination reveals that there are still traces of local cell action caused by the precipitate which alternately slowly forms and flakes off.

The action of the precipitate is further revealed in the following experiment. When the platinum wire is placed near the edge of one specimen giving very uneven current distribution over the surface of the specimen, the precipitate forms on only one half of the specimen (the half away from the wire) while the other half remains clear. Hydrogen bubbles are evolved only on the side covered by the precipitate.

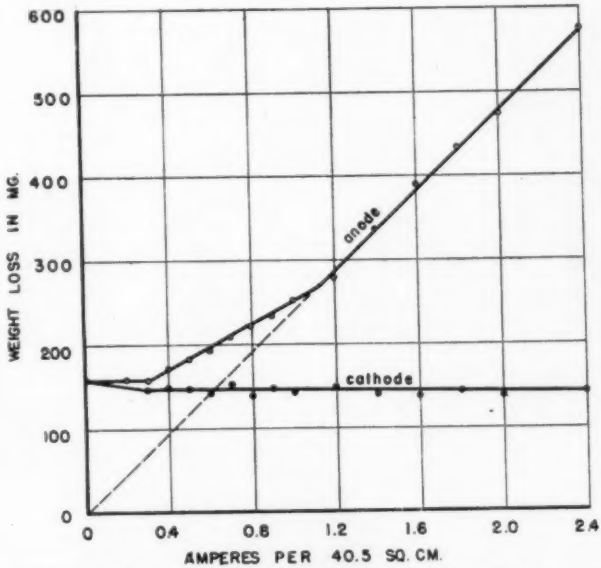

FIG. 14. The effect of an external current on the dissolution of aluminum in 0.30N sodium hydroxide at 23°C. All runs 45 min. Weight-loss in mg. per specimen (40.5 cm.^{2}).

Slight agitation of a 0.30N solution at a current density of 1.0A increases the anode weight-loss considerably and reduces the cathode weight-loss about 10 mg.

When the c.d. reaches 0.3A in a 0.30N solution a definite decrease in hydrogen evolution is observed at the anode, while at the cathode there is a considerable increase in hydrogen evolution. As the c.d. is increased this effect becomes more pronounced. Breaking the circuit (restoring freely-dissolving conditions) immediately increases evolution at the anode and decreases it at the cathode, until both evolve gas at about the same rate. At 0.9A and over, the anode does not evolve hydrogen when first immersed. After about 10 minutes of immersion a slight precipitate forms and gas is

evolved at the anode at an increasing rate. After 30 minutes, the precipitate flakes off and bubbling ceases.

In 1.00N solutions there is a more continuous change in weight-loss of the anode as the c.d. is increased (Fig. 15). The curve cannot be divided into three parts of different slopes as was possible in the previous case. A c.d. of 2.4A is required to suppress hydrogen evolution at the anode on immersion. After about three minutes a precipitate forms accompanied by very light bubbling, and the gas evolution at the cathode is most

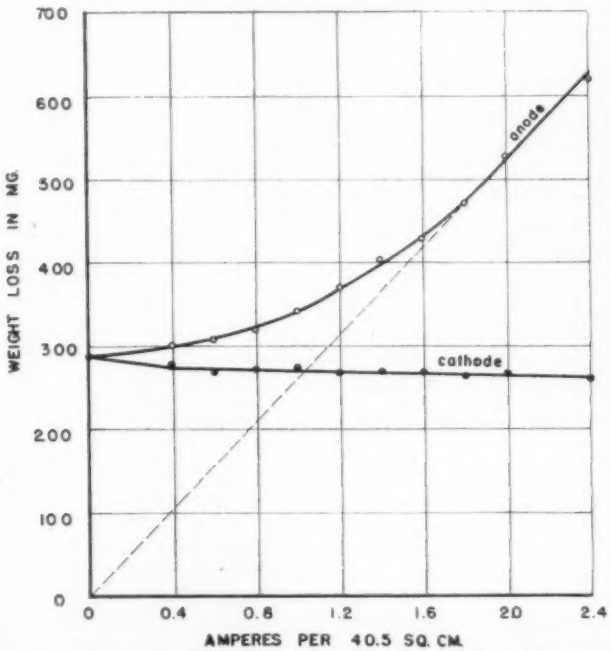

FIG. 15. The effect of an external current on the dissolution of aluminum in 1.00N sodium hydroxide at 23°C. All runs 45 min. Weight-loss in mg. per specimen (40.5 cm.^{2}).

vigorous. It is not possible to obtain a polished appearance at the anode in 1.00N solutions even at a c.d. of 2.4A. A c.d. of 4A produces large bubbles, probably oxygen, at the anode. At current densities above 2.4A the heat evolved becomes so great that it is not possible to control the temperature by the apparatus which was used in these experiments.

Electrode potential measurements were difficult on specimens under the influence of an external current. There was a continual change in potential of both anode and cathode throughout all runs toward more noble (less negative) potentials. In general, the cathode potentials were found

to be more negative than the potentials of the specimens which were made anodic. At higher current densities the potentials fluctuated considerably.

Difference effect

The "difference effect" was calculated for runs in both concentrations of hydroxides studied. All values have been reduced to milligrams. These values and the method of calculation are given in Tables IV and V and are plotted in Fig. 17. At current densities below 0.3A there was no "difference effect" (this may be a result of the sensitivity of the experimental technique).

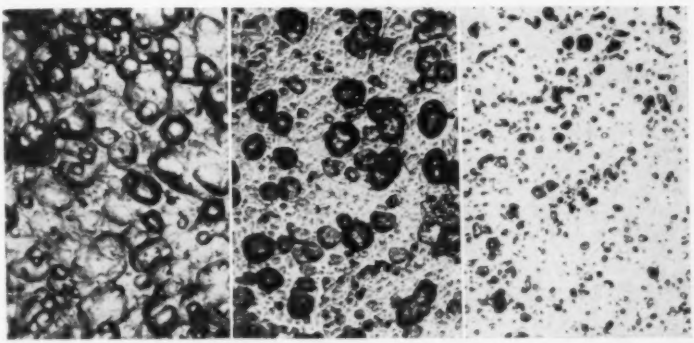

FIG. 16. The effect of increasing anodic current densities on the appearance of the surface of aluminum dissolving in 0.30N sodium hydroxide solutions at 23°C. The precipitate has been removed by wiping. Magnification: 265×. A. Surface of merging craters produced during simple dissolution. B. Surface produced during dissolution at 20 ma. per sq. cm. anodic current density. The number of craters has been reduced. There is dissolution as a result of local action and the external current. Region of the "difference effect." C. Surface produced at 60 ma. per sq. cm. anodic current density. This surface has a polished appearance to the unaided eye. The craters have been eliminated and only small pits remain. These are a result of small quantities of precipitate which alternately form and flake off during dissolution at this current density. Local cell action has practically been suppressed and dissolution is essentially electrochemically equivalent to the external current.

In 1.00N solutions the "difference effect" is linear with the current density up to about 0.8A and, on extrapolation, passes through the origin.

$$\Delta = KI \qquad (X)$$

where K is a constant and I, the current density. This result is in agreement with that obtained by Thiel and Eckell (30) and Müller (28) in 1.00N sodium hydroxide. A current density of 0.8A is equivalent to 20 ma. per cm.^{2} Thiel and Eckell found it to be linear up to 24 ma. per cm.^{2} Müller (28) considers the "difference effect" linear over a larger range and attributes variations in K to experimental inaccuracies. However, when his Δ is plotted against the current density (Müller merely tabulates values of K) it is evident that the "difference effect" is linear up to about 22 ma. per cm.^{2} and then falls off.

In 0.30N solutions the "difference effect" extends to about 1.0A; it is operative only in the region represented by the second portion of the anode curve in Fig. 14. The effect is directly proportional to current density in

TABLE IV. *The difference effect on aluminum in 0.30N sodium hydroxide at 25°*

$W_g - W_e = W_1$ $\qquad$ $W_{1i} = 165.4$

$W_{1i} - W_1 = \Delta$ $\qquad$ $W_e = \dfrac{A \times 45 \times 60 \times 9 \times 1000}{96.500}$

W_{1i} = weight-loss determined under freely dissolving conditions
W_g = total weight-loss observed when external e.m.f. was applied anodically
W_e = weight-loss calculated from current in external circuit
W_1 = weight-loss due to simple dissolution while specimen was made anodic by external e.m.f.
Δ = difference effect

C.D. per specimen	Weight-loss in mg. per 40.5 cm.² in 45 minutes			
	W_g	W_e	$W_g - W_e$	$W_{1i} - W_1 = \Delta$
0.30	162.8	75.5	87.3	78.1
0.40	174.9	100.6	74.3	91.1
0.50	185.0	126.0	59.0	106.4
0.60	195.9	151.0	44.9	120.5
0.70	211.2	176.0	35.2	130.2
0.80	222.3	201.8	20.5	144.9
0.90	237.7	226.8	10.9	154.5
1.00	255.3	252.0	3.3	162.1
1.00*	266.5	252.0	14.5	150.9*

* With mild agitation.

TABLE V. *The difference effect on aluminum in 1.00N sodium hydroxide at 25°*

All runs 45 minutes

C.D. per specimen	W_g	W_e	$W_g - W_e = W_1$	$W_{1i} - W_1 = \Delta$
0.40	303.0	100.6	202.4	87.6
0.60	310.8	151.0	159.8	130.5
0.80	320.6	201.8	118.8	170.6
1.00	344.0	252.0	92.0	198.0
1.20	372.2	302.0	70.2	219.8
1.40	406.3	352.0	54.3	235.7
1.60	431.5	402.5	29.0	261.0
1.80	471.2	452.0	19.2	270.8
2.00	528.2	504.0	24.2	265.8
2.40	620.3	605.0	15.3	274.7

$W_{1i} = 290.0$.

this range. However, on extrapolation the line does not pass through the origin.

$$\Delta = K'I + N \qquad \text{(XI)}$$

where N is the intercept at zero current density.

When the "difference effect" is complete, $W_1 = 0$ and dissolution by local-cell action has ceased, making $\Delta = W_{1i}$. Therefore, the limiting value of the "difference effect" is W_{1i}. This limiting value is reached in 0.30N solution within the accuracy of these experiments.[15]

In 1.00N solutions the limiting value is approached but is not reached at the current densities studied. Even at 2.4A, there is no polishing action on the specimens and the precipitate is the usual powdery type rather than the flaking type observed in the runs using 0.30N solutions.

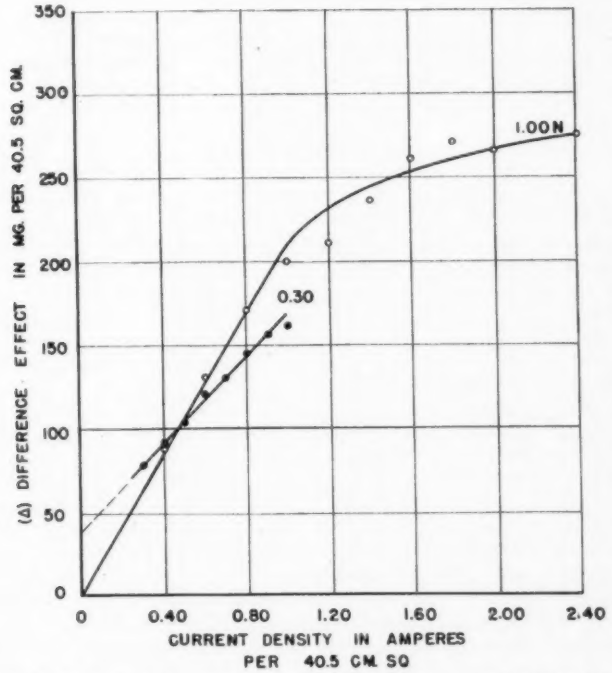

FIG. 17. The effect of current density on the "difference effect" at 23°C.

Discussion

When a current flows in local cells, polarization of the local anodes or cathodes or both (depending on the metal and the solution) may take place. The anodes polarize to more noble potentials and the cathodes to more negative potentials. Brown and Mears (39) have given two equations for local-cell conditions on the assumption that the resistance of the metallic paths and the resistance of the liquid can be neglected.

[15] $W_{1i} = 165.5$ and $\Delta_1 = 155.0$

$$E'_a - \phi_a\left(\frac{I_a}{A_a}\right) = E'_c + \phi_c\left(\frac{I_c}{A_c}\right) \qquad \text{(XII)}$$

and

$$I_c = I_a + I_x \qquad \text{(XIII)}$$

In these equations E'_a and E'_c are the open-circuit potentials of the local anodes and cathodes, A_a and A_c are the areas of the local anodes and cathodes respectively, ϕ_a and ϕ_c are the polarizing functions, I_a the current from the local anode, I_c the current from the local cathode, and I_x the external current. It was further shown by these authors that, for cathodic protection, the anodic current I_a must be zero or be reversed in direction. Thus, when $I_x = 0$, equation (XII) becomes

$$E'_a = E'_c + \phi\left(\frac{I_c}{A_c}\right). \qquad \text{(XIIa)}$$

The local cathodes must be polarized to the open-circuit potentials of the local anodes by an external current for complete protection.

If equation (VIII) of the "difference effect" is converted from volumes of hydrogen evolved per unit of time to equivalent current density[16] we have

$$I_g - I_c = I_1 \qquad \text{(VIIIa)}$$

$$I_W - I_1 = \Delta. \qquad \text{(IXa)}$$

where I_c, I_x = external current
I_g, I_a = current responsible for total weight-loss, a sum of the external current and the local cell current
I_1, I_c = local cell current

Therefore,

$$I_c = I_a - I_x \qquad \text{(VIIIb)}$$

A comparison of equations (XIII) and (VIIIb) reveals that they are identical except for the sign of the external current. This is in agreement with experiment. To protect a metal cathodically, it is connected to a more anodic metal, and to produce a (positive) "difference effect" the metal is connected to a more cathodic electrode or equivalent source of external current.

The limiting condition of the "difference effect" is given when I_1 (or I_c) is reduced to zero. Equation (XII) then is given by

$$E'_c = E'_a - \phi_a\left(\frac{I_a}{A_a}\right). \qquad \text{(XIIb)}$$

Thus, in order to reach the limiting value of the "difference effect," the local anodes must be polarized to the open-circuit potential of the local cathodes. At this point local-cell action ceases and the weight-loss is equivalent to the applied current ($I_g = I_c$).[17]

[16] This equivalence was first pointed out by Müller and Löw (40).

[17] Straumanis (37, 41, 42) and Wesley (43) have previously suggested that the "difference effect" is caused by anodic polarization.

The above relationships do not imply that any given metal may be completely protected or dissolved anodically by merely reversing the external current. Whether a surface can be polarized to the open-circuit potentials of the local anodes or cathodes depends on the nature of the metal and the solution, temperature, and concentration.

Inspection of the equations (VIIIa and IXa) for the "difference effect" reveals that it may become negative in two ways. Since for any run I_e and I_H are fixed, the "difference effect" may be negative as a result of reversing the direction of the external current, i.e., making the specimen under consideration cathodic, or, when the effect of making the specimen anodic is a large increase in I_g. This latter condition has been related to the break-down of a film by Kroenig and Uspenskaja (35). To avoid confusion, it is suggested that the expression "negative difference effect" be used only when it is a result of a large value of I_g and that, if the "difference effect" is negative as a result of a reversal of the external current, the term "cathodic protection" be applied.

In 0.30N (pH = 13.22) solutions at 23°C. local-cell action can be reduced to zero and the limiting value of the "difference effect" can be reached. On the basis of the above considerations, this indicates that in such solutions the local anodes can be polarized to the open-circuit potential of the local cathodes (probably the precipitate in this case). The polarizibility of the local anodes decreases rapidly with increasing pH (Fig. 13). Therefore, it should become more difficult (or impossible) to reach the limiting value of the "difference effect" in more concentrated solutions. This is in agreement with the results on the "difference effect" obtained in 1.00N solutions at 23°C. (pH = 13.58). At this concentration the limiting value of the "difference effect" was not reached within the current densities studied.

Equation (X) has been derived independently by Straumanis (37, 41, 42) on the basis of Palmaer's (44)[18] original equation for local-cell action and the equation for the polarization curve (VII) and by Müller (40, 45) on the basis of his pore theory. Both authors assumed a constant rate of dissolution. Experimentally, equation (X) has been shown to apply in only two cases: for zinc dissolving in 0.50N hydrochloric acid and for aluminum dissolving in 1.00N sodium hydroxide. It is probable that equation (X) represents the purely electrochemical aspect of the "difference effect" and that the derivations of Müller and Straumanis are both descriptive of the electrochemical basis of the phenomenon of dissolving metals, if the fact that the dissolution rate may change with time (itself an electrochemical phenomenon) is taken into consideration.

In the present investigation it was found that the "difference effect" in 0.30N solution has an intercept at zero current density as given in equation (XI). This condition has not been previously described.[19] Under "Ex-

[18] $V = \frac{k(E' - e)}{r}$, where V is the volume of hydrogen evolved during a given period, $(E' - e)$, the potential difference of the local cell, and r, the resistance of the local cell.

[19] There is possibly one exception to this. In the original publication on the "difference effect" by Thiel and Eckell (30) there is a footnote giving values of Δ at two current densities in 0.50N sodium hydroxide for aluminum. When these two points are plotted, the line connecting them does not pass through the origin but has an intercept on the Δ-axis. Neither Thiel and Eckell nor subsequent investigators have taken issue with this footnote.

perimental" a run was described in which mild agitation was used (to aid in temperature control) while the specimen was made anodic. The result was that the anode weight-loss increased considerably, increasing W_o, which, in turn, decreases Δ. Thus in 0.30N solutions there are factors in addition to electrochemical effects, probably diffusion phenomena.

THE MECHANISM OF DISSOLUTION PROPOSED ON THE BASIS OF THE PRESENT STUDY

On the basis of the experimental results of the present study, the dissolution of aluminum in a large volume of sodium hydroxide solution may be described as follows. The alloying constituents (impurities) in the aluminum form the cathode of local cells of which the aluminum matrix is the anode. The initial dissolution rate is a result of the action of these and any other cells, such as those caused by grain boundaries, etc. At the anodes aluminum goes into solution, while at the cathodes an equivalent quantity of hydrogen is evolved. As soon as some metal has dissolved, a black precipitate forms on the surface of the aluminum. This precipitate consists primarily of compounds of the impurities, hydroxides of iron and copper, interspersed perhaps with metallic deposits of these metals.

The precipitate acts as a cathode.[20] The progressive growth of the precipitate increases the total cathodic area, and, since the anodic area is not greatly diminished, the current density at the local anodes increases. As the weight-loss is directly proportional to the anodic current density, the dissolution rate is increased.[21] Increasing the anodic current density causes anodic polarization towards more noble potentials. The current density at the cathodes remains constant, and they do not polarize appreciably. As a result of anodic polarization, the potential difference of the local cells is decreased in proportion to the anodic current density.[22] For this reason the rate of dissolution increases at a decreasing rate until finally a constant rate and potential are reached. At this point, the effective cathodic area no longer increases. This may indicate that the precipitate now grows in depth only.

Thus the dissolution of aluminum in sodium hydroxide is under mixed control with the cathodic processes predominating. The effects of temperature and agitation indicate that the rate-controlling reaction has the properties of a homogeneous chemical reaction. This rate-determining process is probably one of the steps in the series of reactions in which hydrogen ions from the solution are transformed to hydrogen gas at the cathodes. Diffusion effects do not appreciably influence the rate of dissolution under freely dissolving conditions.

[20] There is now a three-electrode system at the surface, anodic areas and two kinds of cathodic areas, one on the metal and one the precipitate.

[21] This is in contrast to the theory of Straumanis (17) in which the precipitate is considered a retarding factor.

[22] The equations for the rate of dissolution developed by Evans (25) and Tammann (20) do not provide for polarization effects. Deviations from their equations are attributed to non-adherence to the surface of the precipitate. The equations (V and Va) are assumed to apply to the "hydrogen evolution" type of dissolution, which includes aluminum in sodium hydroxide. However, the data with which these equations have been compared were obtained in acid solutions only.

The effect of temperature and concentration on the dissolution rate is two-fold. These variables affect the rate-determining or sluggish reaction at the cathodes and also influence the polarization of the anodes.

When the dissolving aluminum is made cathodic by an external current, the rate of dissolution is decreased only slightly. This is probably an indication that one of the two types of cathodes does not polarize appreciably (the precipitate). Making the dissolving aluminum anodic polarizes the local anodes and, as a result, decreases the potential difference of the local cells. Local-cell action is thus gradually eliminated. When the local anodes have been polarized to the open-circuit potential of the local cathodes, local-cell action ceases. The surface is now equipotential, and the weight-loss is electrochemically equivalent to the quantity of current passing through the cell.

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Any discussion of this paper will appear in the discussion section of Volume 93 of the Transactions of this Society.

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A DETERMINATION OF THE FREE ENERGY OF FORMATION OF THE MANGANOUS ION FROM THERMAL DATA[1]

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ABSTRACT

Heats of solution of manganese in HCl, heats of dilution of $MnCl_2$, and heats of mixing of $MnCl_2$ and HCl, and of $MnSO_4$ and H_2SO_4 were determined, the figures obtained being combined with existing data to give the heat of formation of manganese chloride tetrahydrate, and, finally, the free energy of formation of the manganous ion.

INTRODUCTION

The need for a value for the standard potential of manganese, or for the free energy of formation of the aqueous manganous ion, more reliable than those available at present, soon becomes apparent in any electrochemical studies involving the ion. For example, calculations of the standard potential of the manganese dioxide-manganous ion couple in acid solution, based on published values for the standard potential of manganese (19, 22, 32) make it clear that either the latter values are too low, or those quoted for the manganese dioxide potential (3, 19) are too high.

A literature search covering the last 15 years has revealed sufficient data for calculating the free energy of the manganous ion from the solubility products of sparingly soluble salts but each calculation has at least one very doubtful step. A more reliable procedure, the determination from the activity product of the chloride, has been attempted here. As much use as possible has been made of recent data obtained by the U. S. Bureau of Mines, the missing information being supplied by direct experiment. The heat of solution of manganese metal in HCl, as well as several heats of dilution and mixing, have been determined and combined with the known heat of solution of $MnCl_2 \cdot 4H_2O$ to obtain the heat of formation of the latter salt.

[1] Manuscript received January 19, 1948. This paper prepared for delivery before the Columbus, Ohio Meeting, April 14 to 17, 1948.

EXPERIMENTAL

The manganese metal was the brittle variety (α Mn) prepared electrolytically. Polarographic analysis showed it contained less than 0.1 per cent of metals more electropositive than manganese, while gravimetric analysis indicated 99.9 per cent Mn. The solutions of $MnCl_2$, $MnSO_4$, HCl, and H_2SO_4 were of analytical quality, their concentrations being checked by the manganese pyrophosphate gravimetric method.

The calorimeter consisted of a Dewar flask of 750 ml. capacity fitted with a cover similar to that described by White (35) and immersed in a water bath thermostatically controlled to 25 ± 0.02°C. Its thermal leakage modulus was 0.002°C. per minute per degree of thermal head. The stirrer was of the vane type driven at a constant speed of 100 r.p.m. Temperature changes were followed by means of a mercury thermometer which could be read to 0.002°C., but the actual calibration was conducted electrically. A Tinsley vernier potentiometer, standard resistances, and a standardized time-piece were used, the electrical heating being maintained over the same temperature range as occurred in the reaction. The manganese metal and the manganous chloride solutions were contained in fragile glass bulbs weighted with platinum wire and placed at the bottom of the calorimeter. These were broken by depressing the stirrer.

As a check on technique and precision, the heat of solution of magnesium (Kahlbaum, redistilled) in normal HCl was determined, the results agreeing to within 0.25 per cent of the figure given by Shomate and Huffman (29).

The heat of solution of Mn in HCl

The reaction between finely-powdered Mn and acid of concentration $HCl \cdot 20H_2O$ is very vigorous. Large pieces of the brittle metal were therefore crushed and a size fraction of 1–2 mm. selected which gave a reaction time of about 5 minutes when the molar proportions reacting were 1 Mn to 100 of $HCl \cdot 20H_2O$.

The results obtained for the heat of the reaction were 52.13, 52.20, 51.99, 52.03: mean 52.09 ± 0.10 kilocalories per mole of Mn. The uncertainty, 0.10, is taken as twice the standard deviation of the mean. The correction due to heat loss by evaporation caused by the hydrogen evolved follows that proposed by Maier (21) who assumed that in the solution of Zn in HCl all the hydrogen passed out of solution and was saturated with water vapour. The vapour pressure over the HCl solution is 20.5 mm. which leads to a correction of 0.29 kilocalories per mole of hydrogen, with an error of about 10 per cent. The corrected value for the reaction heat (ΔH_1) is thus 52.38 kilocalories with an uncertainty of $\sqrt{0.10^2 + 0.03^2} = 0.10$ kilocalories.

Heats of dilution of $MnCl_2 \cdot 40H_2O$

The heat evolved in the dilution of $MnCl_2 \cdot 40H_2O$ to $MnCl_2 \cdot 300H_2O$ (ΔH_3) was determined as 1.42, 1.36: mean 1.39 ± 0.06 kilocalories per mole $MnCl_2 \cdot 40H_2O$. Similarly, the heat evolved in the dilution of $MnCl_2 \cdot 40H_2O$ to $MnCl_2 \cdot 1600H_2O$ was determined as 1.79, 1.77: mean 1.78 ± 0.02 kilocalories. The reason for selecting these dilution ranges will be clear when the skeleton equations required for the summations are considered.

Heat of mixing of $MnCl_2 \cdot 40H_2O$ and $HCl \cdot 20H_2O$

Three determinations of the heat content change ($-\Delta H_2$) occurring on

mixing the above solutions in the molar proportions of 1 to 98 were made, the results being 0.23, 0.21, 0.25: mean 0.23 ± 0.02 kilocalories.

Heat of mixing of $MnSO_4 \cdot 108H_2O$ and $H_2SO_4 \cdot 108H_2O$

The proportions used here were 1 mole of $MnSO_4 \cdot 108H_2O$ to 48.05 moles of $H_2SO_4 \cdot 108H_2O$ and the results of the determinations were 1.94, 2.15: mean 2.04 ± 0.20 kilocalories ($-\Delta H_{12}$).

DISCUSSION OF EXPERIMENTAL VALUES

Könneker and Biltz (16) obtained 50.7 kilocalories for the heat of solution of manganese metal in $HCl \cdot 20H_2O$ at 20–22°C. They do not state the proportions of metal and acid used, but from the quoted water value of their calorimeter and contents and from Biltz' earlier experiments it would seem that the molar proportions varied between about 1 to 75 and 1 to 125. Their result, however, seems incompatible with the value for the heat of solution of Mn in H_2SO_4, which was obtained by Southard and Shomate (30), and which is undoubtedly more accurate. (See section on entropy of Mn^{++}.)

The only recent value for the heat of dilution of manganous chloride is that of Kapustinsky (8), who obtained $\Delta H = -0.48$ for the reaction

$$MnCl_2 \cdot 55.5H_2O + 1054 \cdot 5H_2O = MnCl_2 \cdot 1110H_2O.$$

Here again the heat content change differs more than would be expected from the value −1.78 for the dilution

$$MnCl_2 \cdot 40H_2O + 1560H_2O = MnCl_2 \cdot 1600\ H_2O.$$

The heats of mixing of HCl and some bivalent metal chlorides have been shown by Richards and Burgess (25) to be negligible. Their solutions, however, were about 10 times as dilute as those used here. On the other hand, the heat of mixing of H_2SO_4 and $MnSO_4$ is appreciably endothermic because of the conversion of most of the sulphate ions to bisulphate ions. Harned and Owen (7) quote two widely differing values, −5.2 and −2.2 kilocalories for the heat content change in the ionization

$$HSO_4^- \rightarrow H^+ + SO_4^{--}.$$

THE FREE ENERGY OF FORMATION OF THE MANGANOUS ION

The heat of formation of $MnCl_2 \cdot 4H_2O$

This is obtained by the following summation:

		ΔH
(1) $Mn + 100(HCl \cdot 20H_2O)$	$= MnCl_2 \cdot 98HCl \cdot 200H_2O + H_2$	−52.38 ±0.10
(2) $MnCl_2 \cdot 98HCl \cdot 2000H_2O$	$= MnCl_2 \cdot 40H_2O + 98\ (HCl \cdot 20H_2O)$.	−0.23 ±0.02
(3) $MnCl_2 \cdot 40H_2O + 260H_2O$	$= MnCl_2 \cdot 300H_2O$.....	−1.39 ±0.06
(4) $MnCl_2 \cdot 300H_2O$	$= MnCl_2 \cdot 4H_2O + 296H_2O$	+1.73 ±0.02
(5) $H_2 + Cl_2 + 40H_2O$	$= 2(HCl \cdot 20H_2O)$.....	−78.19 ±0.10
(6) $4H_2 + 2O_2$	$= 4H_2O$	−273.27 ±0.04
(7) $Mn + Cl_2 + 4H_2 + 2O_2$	$= MnCl_2 \cdot 4H_2O$	−403.73 ±0.16

The heat of solution, ΔH_4, has recently been determined by Voskresenskaya and Ponomareva (33) while Rossini's (26, 27) values have been used for ΔH_5 and ΔH_6.

The entropy and free energy of formation of $MnCl_2 \cdot 4H_2O$

The standard entropy of this salt has not been reported, but it can be calculated by making use of the observation of Kelley and Moore (13) that for six different salts the difference in entropy between the hydrated and anhydrous form is 10.75 ± 0.32 units per mole of water, irrespective of the number of moles of water present. Using Kelley and Moore's (12) value of 28.0 ± 0.8 for the entropy of $MnCl_2$, that of the tetrahydrate becomes $28.0 + (4 \times 10.75) = 71.0 \pm 1.5$ entropy units. This value combined with the entropies of the elements listed in Kelley's compilation (10) leads to a value of -212.9 ± 1.5 units for the entropy of formation, ΔS^0_{298}.

The free energy of formation is then given by

$$\begin{aligned} \Delta G^0 &= \Delta H^0 - T\Delta S^0 \\ &= -403.73 - (298.16 \times -0.2129) \\ &= -340.27 \pm 0.48 \text{ kilocals. per mole.} \end{aligned}$$

The free energy of solution of $MnCl_24H_2O$

Dawson and Williams (4) obtained a figure of 6.15 molal for the solubility of the salt at 25°C., in fair agreement with Benrath's (1) determination of 6.05 molal. The activity coefficients of concentrated $MnCl_2$ solutions have recently been determined by Stokes (31) from whose data the quantities $\gamma_\pm = 1.92$ and $a_w = 0.563$ are obtained for molality 6.10 by interpolation. The activity coefficients of $MnCl_2$, unlike those of $CaCl_2$ and $MgCl_2$, do not vary much with concentration in this region; errors in fixing the molality at saturation, therefore, are relatively unimportant. Considering the equilibrium as represented by

$$MnCl_24H_2O = Mn^{++} + 2Cl^- + 4H_2O$$

it follows that

$$\begin{aligned} \Delta G^0 &= -RT \ln 4(m\gamma_\pm)^3 a_w^4 \\ &= -1364 \log_{10}[4(1.92 \times 6.10)^3 \cdot (0.563)^4] \\ &= -3.83 \text{ kilocals., with an estimated uncertainty of } 0.04 \text{ kilocals.} \end{aligned}$$

The free energy of formation of Mn^{++}

From the results of the two previous sections and from the free energies of the chloride ion (20) and water (27, 10), the free energy of formation of Mn^{++}, $\bar{G}^0_{Mn^{++}}$, is obtained thus,

$$\begin{aligned} \bar{G}^0_{Mn^{++}} &= \Delta G^0 - 2\bar{G}^0_{Cl^-} - 4G^0_{H_2O} + G^0_{MnCl_24H_2O} \\ &= -3.83 - 2(-31.37) - 4(-56.70) - 340.27 \\ &= -54.56 \pm 0.53 \text{ kilocalories.} \end{aligned}$$

THE ENTROPY OF THE MANGANOUS ION

Some of the experimental data may be combined in another way to obtain the heat of formation and hence the entropy of the manganous ion. The heat content change required is that involved in the ionization $Mn = Mn^{++} + 2e$, which, by the definition of the standard state, is the same as that in the reaction $Mn + 2H^+ = Mn^{++} + H_2$, or in the reaction Mn

$+ 2(HCl \cdot \infty H_2O) = MnCl_2 \cdot 2 \infty H_2O + H_2$. The heat content change of the latter follows from the summation:

		ΔH
(1) $Mn + 100(HCl \cdot 20H_2O)$	$= MnCl_2 \cdot 98HCl \cdot 2000H_2O + H_2$	-52.38 ± 0.10
(2) $MnCl_2 \cdot 98HCl \cdot 2000H_2O$	$= MnCl_2 \cdot 40H_2O + 98(HCl \cdot 20H_2O)$	-0.23 ± 0.02
(8) $2(HCl \cdot \infty H_2O)$	$= 2(HCl \cdot 20H_2O) + 2(\infty - 20H_2O)$	$+1.70 \pm 0.10$
(9) $MnCl_2 \cdot 40H_2O + 2(\infty - 20)H_2O$	$= MnCl_2 \cdot 2 \infty H_2O$	-2.18 ± 0.10
(10) $Mn + 2(HCl \cdot \infty H_2O)$	$= MnCl_2 \cdot 2 \infty H_2O + H_2$	-53.09 ± 0.17

The heat of dilution, $-\Delta H_8$, is taken from Rossini (26) while ΔH_9 is the sum of the experimental value (1.78) of the heat of dilution to a dilution of 1600 H_2O, and an estimated value from dilution 1600 to infinite dilution. The heats of dilution of $MnCl_2$ solutions measured here are greater than those of other 2–1 type chlorides reported by Lange and Streeck (17). In the more dilute range the differences will be less so that from the latter's results it seems that a value of 0.40 ± 0.10 can probably be assumed, making a total of -2.18 for ΔH_9.

An attempt was next made to confirm the value of ΔH_{10} by using corresponding data for sulphuric acid and manganous sulphate based on Southard and Shomate's (30) value for the heat of solution of Mn in normal H_2SO_4.

		ΔH
(11) $Mn + 49.05\ (H_2SO_4 \cdot 108H_2O)$	$= MnSO_4 \cdot 48.05H_2SO_4 \cdot 5299H_2O$	-54.4
(12) $MnSO_4 \cdot 48.05H_2SO_4 \cdot 5299H_2O$	$= MnSO_4 \cdot 108H_2O + 48.05(H_2SO_4 \cdot 108H_2O)$	-2.0
(13) $H_2SO_4 \cdot \infty H_2O$	$= H_2SO_4 \cdot 108H_2O + (\infty - 108)H_2O$	$+4.5$
(14) $MnSO_4 \cdot 108H_2O + (\infty - 108)H_2O$	$= MnSO_4 \cdot \infty H_2O$	-1.5
(15) $Mn + H_2SO_4 \cdot \infty H_2O$	$= MnSO_4 \cdot \infty H_2O + H_2$	-53.4

The value of ΔH_{11} is known with high precision ($\pm$ 35 cals.) but the reliability of the heats of reactions 13 and 14 is much less. The heat of dilution of H_2SO_4 is the 18° value chosen by Bichowsky and Rossini (2), while that for reaction 14 is Lange, Monheim, and Robinson's (18) value for the heat of dilution of $CuSO_4$ over the same dilution range at 25°C. As justification for the use of this figure it should be mentioned that Plake (24) showed that the heats of dilution of $CuSO_4$ and $MnSO_4$ at 20°C., over the range 0.25 m. to 0.0002 m. differed by less than 100 calories. Lange, Monheim, and Robinson also determined the heat of dilution of H_2SO_4 at 25°C. but their measurements do not extend to such concentrated solutions as are used here. Their values in the more dilute range are considerably higher than the 18° values of Bichowsky and Rossini. In the circumstances, better agreement between ΔH_{10} and ΔH_{15} could probably not be expected.

The entropy change in the reaction $Mn + 2H^+ = Mn^{++} + H_2$ is then $1000/298.16\ (54.56 - 53.09) = 4.9 \pm 1.9$ units, from which the entropy of the manganous ion is derived as -18.7 ± 1.9 units. Kapustinsky (8) obtained -19.1 using data for the heat and free energy of formation of $MnCO_3$. His derived value for the heat of formation of the manganous ion is, however, much lower than that obtained here. The entropy of Mn^{++} thus appears to be quite appreciably different from the entropies of

the neighboring transition elements (19), viz., Fe^{++}, -25.9; Cu^{++}, -26.5; Zn^{++}, -25.7.

CALCULATIONS OF THE FREE ENERGY OF FORMATION OF MANGANOUS ION FROM OTHER DATA

Calculations based on determinations of the solubility of MnS or of $MnCO_3$ are each open to objection. Maier (22) and Kelley (9) reviewed the data on MnS and the latter pointed out many inconsistencies. Since then (1937) Könneker and Biltz (16) have obtained a value for the heat of formation of green MnS which should be more reliable than previous ones. Having used a solution method, they were able to ensure that their material agreed with the stoichiometric formula MnS. The difficulty of interpreting Weigel's (34) solubility data for green MnS still exists, however. If Maier's (22) method for calculating the free energy of solution of MnS is used, the free energy of formation of the manganous ion is calculated as -51.4 kilocalories, but if Kolthoff's (15) method is used the figure is some 10 kilocalories higher. Similarly, Kelley and Anderson (11) have shown that there are two self-consistent sets of data for the heat of formation of $MnCO_3$ differing by about 10 kilocalories. The discrepancy here can probably be partly explained by the differences in heat content between freshly precipitated and aged crystalline substances, which Fricke (6) has shown may often amount to several kilocalories.

Recent determinations of the solubility of $Mn(OH)_2$ enable a calculation of $\bar{G}^\circ_{Mn^{++}}$ to be made which is less open to the above objection, since the free energy of solution and the free energy of formation of $Mn(OH)_2$ can be obtained from similar precipitation reactions, so that errors due to the above cause should tend to cancel. Fox, Swinehart, and Garrett (5) using the conductimetric method obtained 1.6 to 2.8×10^{-13} for the solubility product, while Näsänen (23) using the potentiometric method obtained 1.9×10^{-13}. Taking a mean of 2.0×10^{-13} one arrives at 17.3 kilocalories for ΔG°, where

$$\Delta G^\circ = \bar{G}^\circ_{Mn^{++}} + 2\bar{G}^\circ_{OH^-} - G^\circ_{Mn(OH)_2}.$$

The only value available for the heat of formation of $Mn(OH)_2$ is that calculated by Bichowsky and Rossini (2) from Thomsen's data. For the precipitation

(16) $MnSO_4 \cdot 400H_2O + 2(KOH \cdot 200H_2O) = Mn(OH)_2 + K_2SO_4 \cdot 800H_2O$

he found $\Delta H = -4.91$ kilocalories at 18°C. The recent value of -254.3 kilocalories for the heat of formation of MnSO (30) is 3 kilocalories higher than the old (and only) value available to Bichowsky and Rossini, which leads to a correspondingly higher value for the heat of formation of $Mn(OH)_2$. The heat of formation of $MnSO_4 \cdot 400H_2O$ is obtained from the following summation:

		ΔH
(17) $MnSO_4 + 49.05(H_2SO_4 \cdot 108H_2O)$	$= MnSO_4 \cdot 49.05H_2SO_4 \cdot 5299H_2O$	-11.6
(18) $MnSO_4 \cdot 49.05H_2SO_4 \cdot 4299H_2O$	$= MnSO_4 \cdot 108H_2O +$ $49.05\ (H_2SO_4 \cdot 105.8H_2O)$	-2.0
(19) $MnSO_4 \cdot 108H_2O + 292H_2O$	$= MnSO_4 \cdot 400H_2O$	-0.2
(20) $49.05(H_2SO_4 \cdot 105.8\ H_2O) + 108H_2O$	$= 49.05(H_2SO_4 \cdot 108H_2O)$	-0.3
(21) $Mn + S + 2O_2$	$= MnSO_4$	-254.2
(22) $Mn + S + 2O_2 + 400H_2O$	$= MnSO_4 \cdot 400H_2O$	-268.3

The heats of reactions 17 and 21 are given by Southard and Shomate (30); the heat of mixing 18 is assumed to be the same as that of reaction 12, while ΔH_{19} and ΔH_{20} are obtained from the same sources as ΔH_{14} and ΔH_{13}. Small temperature corrections can be made to the heats of formation of $KOH \cdot 200H_2O$ and $K_2SO_4 \cdot 800H_2O$ given by Bichowsky and Rossini so that the only remaining 18° values are the two small quantities ΔH_{16} and ΔH_{20}. The newly calculated heat of formation of $Mn(OH)_2$ then becomes −166.8 kilocalories.

The entropy has not been determined, but a value can be calculated from the entropy of MnO and the entropies of hydration of similar oxides, thus,

Metal	$S^\circ_{M(OH)_2}$	S°_{MO}	$S^\circ_{M(OH)_2} - S^\circ_{MO}$
Mg	15.1	6.6	8.5
Mn	—	14.4	—
Ca	17.4	9.5	7.9
Cd	21	13.1	8

Kireev (14) has calculated the entropies of five other bivalent hydroxides from the entropy of formation from the elements considering them as monatomic ideal gases. This permits a calculation of five more values for $S^\circ_{M(OH)_2} - S^\circ_{MO}$. It is found that these five, together with the above three experimental values, all lie in the range 8.2 ± 1.1 units. $S^\circ_{Mn(OH)_2}$ thus becomes $14.4 + 8.2 = 22.6$ units, the entropy of formation of $Mn(OH)_2$ −65.2 units, and the free energy of formation −147.4 kilocalories.

The free energy of the hydroxyl ion is obtained from Harned and Owen's (7) value for the ionic product of water and Rossini's (27) value for the free energy of formation of water, as $\bar{G}^\circ_{OH} = -37.6$ kilocals. Then

$$\begin{aligned}\bar{G}^\circ_{Mn^{++}} &= \Delta G^\circ - 2\bar{G}^\circ_{OH^-} + G^\circ_{Mn(OH)_2} \\ &= 17.3 + 75.2 - 147.4 \\ &= -54.9 \text{ kilocals., with an estimated uncertainty of about 1 kilocal.}\end{aligned}$$

THE STANDARD POTENTIAL OF MANGANESE

The standard potential of the metal is given by

$$E^0_{Mn^{++},Mn} = \frac{\bar{G}^0_{Mn^{++}}}{2F} = -\frac{54.56}{46.14} = -1.182 \pm 0.012 \text{ volts.}$$

The direct determination of this potential is difficult and there does not appear to have been any attempt at it since Royce and Kahlenberg's (28) investigation in 1926. As Maier (22) has pointed out, the electrolyte concentrations used by them were not clearly stated so that when activity coefficients became available years later they could not be applied with certainty. If Stoke's (31) values for the activity coefficients of $MnCl_2$ are used in the manner suggested by Maier, the standard potential proves to be −1.135 v. The standard potentials of aluminum and of magnesium obtained from cell measurements are lower (less negative) then those calculated from thermal data, and manganese, with its similar tendency towards film formation, may be expected to behave similarly. Most authors of

electrochemical texts either omit all reference to the standard potential of manganese or else prefer some calculated value to that of Royce and Kahlenberg. Among the calculated values one finds quoted figures as low as -1.02 and -1.05 v. It is felt that the above value of -1.18 is nearer the truth than those previously suggested, but confirmation of some of the data by the methods of modern precision calorimetry is clearly required.

SUMMARY

The value found for the free energy of formation of the manganous ion was -54.56 ± 0.53 kilocalories, corresponding to -1.182 ± 0.012 v. for the standard potential. These are appreciably more negative than the values usually quoted. The data also permit an approximate calculation of the entropy of the manganous ion as -18.7 ± 1.9 units. A calculation of the free energy of the manganous ion from existing data on manganous hydroxide provides a value which agrees to within less than 1 per cent of the value -54.56.

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Any discussion of this paper will appear in the discussion section of Volume 93 of the Transactions of this Society.

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INFLUENCE OF ATMOSPHERE FIRING ON THE CATHODOLUMINESCENCE OF ZINC SULFIDE: SILVER TYPE PHOSPHORS[1]

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ABSTRACT

The cathodoluminescent efficiencies and spectral distributions of zinc sulfide: silver and zinc-cadmium sulfide: silver phosphors prepared by firing in various gases were determined. Reducing atmospheres produced phosphors of low efficiency, while oxidizing atmospheres gave rise to highly efficient products. Shifts in spectral distribution also occurred with the various atmospheres. With zinc sulfide: silver phosphors, the shifts were due mainly to oxidation effects. With zinc-cadmium sulfide: silver phosphors, both oxidation effects and selective volatilization of one of the components of the matrix determined the spectral distribution. Results indicate that reproducible samples of zinc sulfide phosphors can be prepared if all the materials used, including the atmosphere, are carefully controlled.

INTRODUCTION

The importance of the gaseous environment during the firing of zinc sulfide type phosphors has been realized by many investigators, and a number of procedures for control have been published (1, 2, 3, 4, 5, 6, 7). In most procedures, oxidation of the samples was to be prevented, although some types of phosphors were found to be most efficient when slight oxidation was permitted (7, 8, 9, 10). It has also been reported that the type of atmosphere affected the particle size of the product (3). Methods advocated to prevent oxidation were: firing in vacuo (Streck); firing in an atmosphere of sulfur, which under the conditions of the experiments was more probably sulfur dioxide (Einig, Zhirov, Kamm); covering the charge with a layer of unactivated zinc sulfide (Kamm); and, firing in hydrogen or hydrogen sulfide (Rothschild, Zhirov). Kamm tried firing in graphite crucibles, but could not prevent oxidation by such means.

No critical comparison of materials fired in a variety of atmospheres to determine the effects of such treatment on cathodoluminescence has yet been published. To determine what effects, if any, such treatment might have, silver-activated zinc sulfides and zinc-cadmium sulfides were fired in the presence of a number of different gases and the cathodoluminescent efficiencies and emission spectra of the resultant phosphors were obtained. Silver activation was chosen because of the commercial importance of these phosphors and the simplicity of the spectral curves. Preliminary investigations have indicated that manganese-activated materials show simple relations as do the silver-activated ones, while copper activation gives rise to the complications reported by Rothschild (7) for photoluminescence.

The program to investigate the results of variations in the preparatory conditions of these phosphors was undertaken because a considerable portion of the theoretical work reported in the literature has been based on

[1] Manuscript received March 19, 1948. This paper prepared for delivery before the Columbus, Ohio Meeting, April 14 to 17, 1948.

materials of uncertain composition, or on phosphors which could not be duplicated exactly. Dielectric properties, emission spectra, trap depths, etc., are severely altered by unsuspected factors introduced during the preparation of the sample unless great care is exercised to control every possible variable. It is hoped that the results obtained from this investigation will persuade theoretical workers in this field to give more serious consideration to the chemical composition of the materials with which they work than has been the custom in the past. It is also hoped that this investigation will provoke a more quantitative study of this nature by other experimentalists.

MATERIALS

Zinc sulfide and zinc-cadmium sulfide

The zinc sulfides and zinc-cadmium sulfides were prepared by a method which is essentially that of Einig (1). It involves the usual fractional precipitation for removal of "heavy" metals, with the final product being precipitated from an acid solution. The final product contained less than 10^{-6} per cent of copper. This was determined in two ways; first, spectrographic analysis failed to detect any traces of copper, and secondly, a fluxed, fired sample gave no trace of green emission when excited by 3650Å radiation at elevated temperatures. A sample prepared in identical fashion, but with the intentional addition of 10^{-6} per cent of copper, showed strong green emission under the method of testing mentioned before. Einig stated that this method of purification completely removes iron, but it is doubtful whether it is entirely removed. It is certainly removed to the extent that it does not act as a poison, since extremely long-persistent copper-activated materials have been produced from sulfides so prepared. The production of such materials would be impossible if iron were present in activator proportions.

The major portion of this work was conducted with the same lots of sulfides which were used in the flux control work to be published elsewhere (11). The results were checked by the use of different lots of zinc sulfide; no differences were observed.

To be certain that no oxy-anions remained in the precipitated sulfides, the activated unfluxed mixture (silver nitrate added to a water slurry of the sulfide, then dried) was fired for one hour at 700°C. in hydrogen sulfide. It had been determined previously that both zinc oxide and zinc sulfate could be quantitatively converted into zinc sulfide by such treatment, and that phosphors made from sulfides so prepared showed no "oxide effects," that is, no shift of wavelength which is caused by oxide incorporation.

In those cases where fluxes were added to materials pretreated with hydrogen sulfide, the additions were made in the dry form lest hydrolysis introduce oxy-anions. The addition of activators and fluxes to untreated sulfides was performed by adding aqueous solutions of the necessary compounds to an aqueous slurry of the sulfides, and then evaporating to dryness.

Fluxes

The same lots of reagent grade sodium and barium chlorides were used in this work as were used in the investigation of fluxing agents (11). It

is shown in that paper that extensive purification of fluxes gave the same results as the use of the above lots of reagent grade chemicals. It is obvious that only selected reagent grade chemicals may be used in this fashion.

Atmospheres

The general procedures which were used for the purification of the gases are shown in Table I.

TABLE I. *Methods of gas purification*

Gas	Source	Oxygen removal	Water removal	CO_2 removal
Nitrogen	Tank	Hot Cu* or Pd on alumina + H_2†	$CaCl_2$ + P_2O_5 or activated alumina	Ascarite + activated BaO
Hydrogen	Tank	Pd on alumina catalyst	Drierite	Activated BaO
Hydrogen sulfide	Tank	(Conc. soln. of $Ba(OH)_2$)‡	$CaCl_2$ + P_2O_5	
Carbon monoxide	Tank	Passed through tube at 1000°C.	Ascarite + BaO	Ascarite + BaO
Ammonia	Tank	Passed through tube at 1000°C.	Ascarite + BaO	Ascarite + BaO
Carbon dioxide	Generated§		Conc. H_2SO_4 + P_2O_5	
Water vapor	Generated	Carried by O_2 free N_2¶		
Carbon disulfide	Distilled CS_2	Carried by dry O_2 free N_2		
Sulfur dioxide	Tank	(Washed soln. H_2SO_3)‡	Drierite + P_2O_5	
Hydrogen chloride	Generated‖		Conc. H_2SO_4 + P_2O_5	

* A total of at least 60 inches of one-inch-diameter tubing filled with copper "wire" maintained at 450-500°C. is necessary for flows of 500 ml./min.

† Palladium on alumina catalyst was contained in two tubes each 30 x 1 in. Ratio of hydrogen to nitrogen was 1:100. Hydrogen was then removed by passing over copper-oxide "wire." When the copper was re-oxidized, tube was swept by nitrogen for a minimum of twelve hours before re-use.

‡ No precautions taken to remove oxygen.

§ Reaction, $Na(HCO_3)_2$ + conc. H_2SO_4. Flask swept free of oxygen before gas used.

¶ Nitrogen passed through flask of boiling water. Water previously boiled to remove air.

‖ Reaction, NaCl + HCl acid + conc. H_2SO_4. Flask swept free of oxygen before gas used.

APPARATUS AND PROCEDURE

A two-tube combustion furnace with manual temperature control was used. The method of firing is shown in Fig. 1. This technique was first adapted to phosphor work by Ward and coworkers (12). The silica-glass combustion tube containing the sample is first swept free of air by passing a rapid flow of the gas under test through the tube for twenty minutes. The tube is then placed in the furnace which previously has been heated to the required temperature. About twenty or twenty-five minutes are required for the combustion tubes to reach temperature equilibrium with the furnace at 1200°C. A flow of 50 to 100 ml./min. of the gas under test is maintained at all times. At the end of the specified time the entire tube is removed from the furnace and the sample allowed to cool in the desired atmosphere. To prevent leaks, all joints in tubes and gas system are sealed with Pyseal cement.

Method of measurement

The cathodoluminescent efficiencies and emission spectra were determined with a defocused electron beam having a current density of 1.5 μa per sq. cm. and an accelerating voltage of 8000 volts. Peak efficiencies and spectral distribution of energy were measured by means of the spectroradiometer described by A. E. Hardy (13). Visual efficiencies were measured with an eye-corrected Weston selenide barrier-layer photocell.

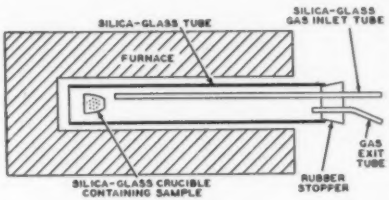

FIG. 1

TABLE II. *Efficiencies of zinc sulfide*
0.015% Ag—1150°
Visual efficiency/peak efficiency

Atmosphere	H_2S pretreated ZnS			Untreated ZnS	
	NaCl flux	NaCl + $BaCl_2$ flux	No flux	NaCl + $BaCl_2$ flux	Peak emission (Angstroms)
Neutral:					
N_2	100/100	—	50/37	110/107	4350 (narrow)
H_2O	96/95	—	—	103/102	4350
HCl	170/126	—	155/126	—	4350
CO	98/82	—	—	104/98	4350
Reducing:					
H_2S	0	—	<10	0	(?)
CS_2	71/61	—	—	—	4275 (narrow)
H_2	82/41	80/44	0	52/70	4300 (narrow)
Oxidizing:					
CO_2	126/98	130/87	65/38	—	4400
SO_2	126/102	120/88	115/95	122/84	4425

DISCUSSION

Table II shows the effects on the cathodolminescence of zinc sulfide: 0.015 per cent Ag caused by firing in various atmospheres at 1150°C. for twenty minutes. Visual cathodoluminescent efficiencies are to the left of the oblique dash and the peak efficiencies to the right of it. Relative units are used. The standard of comparison is the average of three samples prepared from hydrogen-sulfide-pretreated zinc sulfide fluxed by 2 per cent of sodium chloride and fired in nitrogen. The average deviation of the visual efficiencies of these three samples was $\pm$ 6, while the average deviation of the peak efficiencies was $\pm$ 2. As can be seen in Fig. 2, pre-

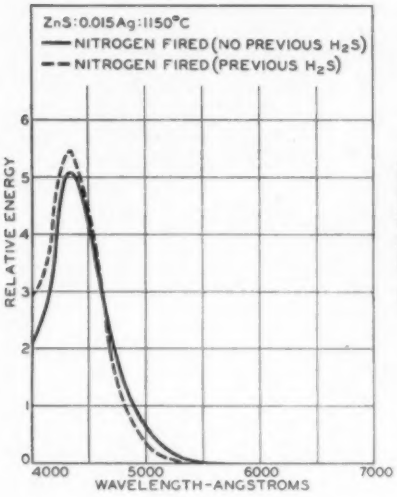

FIG. 2

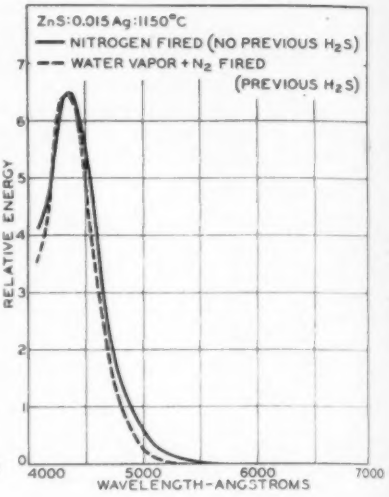

FIG. 3

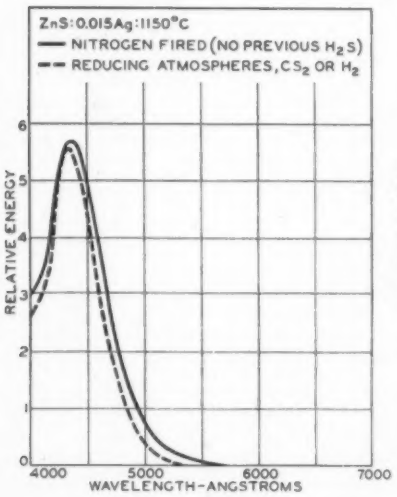

FIG. 4

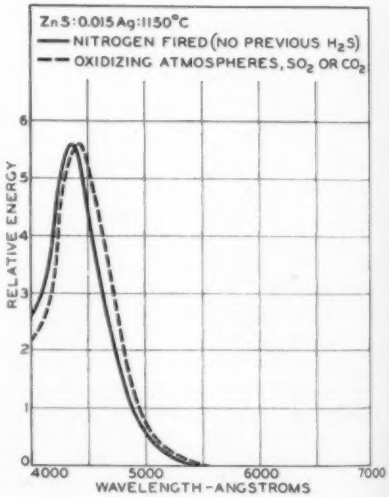

FIG. 5

treated samples have narrower emission bands than samples which are not pretreated. The shifts in spectral distribution caused by firing in water vapor, reducing atmospheres, and oxidizing atmospheres are shown in Fig. 3, 4, and 5, respectively.

Table III gives the same information for hydrogen-sulfide-pretreated zinc-cadmium sulfide (47:53): 0.01 per cent Ag fired at 1000°C. for twenty minutes, but with no flux. The standard is the average of a series fired in nitrogen in which the average deviation of the visual efficiencies was ± 2, while the average deviation of the peak efficiencies was ± 4. Fig. 6, 7, and 8 give the spectral distribution shifts obtained by firing in sulfur dioxide, hydrogen chloride, and carbon monoxide, respectively.

It is readily apparent that considerable variations in both spectral distribution and efficiencies are caused by the use of different atmospheres. With the exception of the samples fired in hydrogen chloride, the changes which occurred in the zinc sulfide phosphors are attributed directly to the incorporation or removal of oxide ions from the base matrix. This hypothesis is substantiated by the following experiment. Zinc oxide was added to samples which previously had been fired under reducing condi-

TABLE III. *Efficiencies of zinc-cadmium sulfide (47:53)*
0.01% Ag—1000°
No flux
Visual efficiency/peak efficiency

Atmosphere	Efficiency	Peak emission (Angstroms)
Neutral:		
N_2	100/100	5590
H_2O	110/114	5630
HCl	130/142	5780
Reducing:		
H_2S	42/38	5580
CS_2	42/41	5580
H_2	*	?
CO	68/73	5530
NH_3	50/55	5530
Oxidizing:		
CO_2	210/178	5680
SO_2	155/175	5680

* Samples inhomogeneous. No measurement possible.

tions, flux added, and the mixtures refired in nitrogen. The peak efficiency of the cathodoluminescence increased by 50 per cent.

This "oxide effect" may be similar to that which occurs in the infrared-sensitive phosphors described by Ward (12). Certain base matrices are much more stimulable by infrared if they contain small proportions of oxide ion, but become more phosphorescent and less efficient under infrared radiation if the oxide content exceeds certain limits. The findings of Ward (14) concerning the sensitivity of the "oxide effect" as a function of activator concentration in the infrared-sensitive phosphors suggest that the same type of investigation might be fruitful in the case of the zinc sulfide types.

The possibility of valence change of silver such as that hypothesized for the dual band of copper (7) does not appear reasonable for this case, although it cannot altogether be excluded. Reducing gases do not cause gray tones in the sample when inspected in white light, so it may be presumed little or no free silver is formed. It is believed that the knowledge

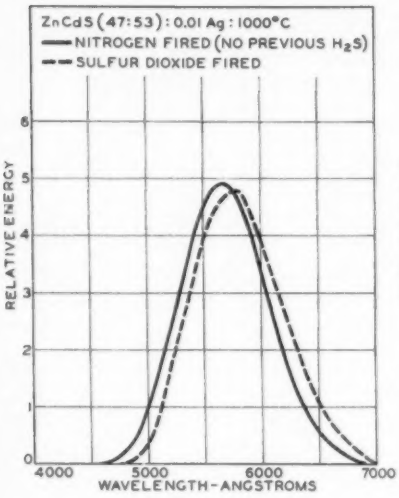

FIG. 6

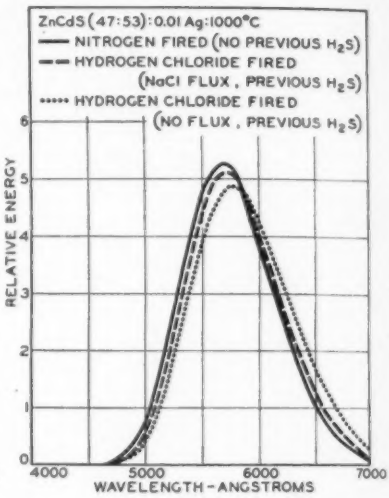

FIG. 7

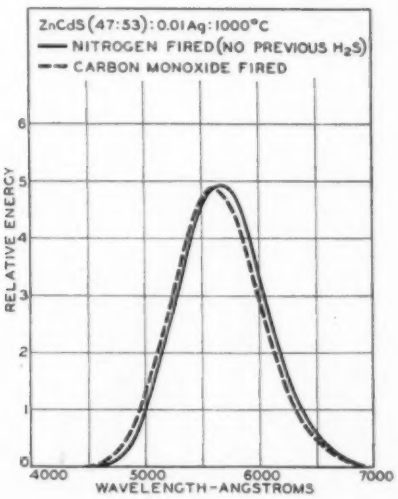

FIG. 8

of the valence states of activators in phosphors is so meager that no hypothesis built upon a valence change concept can yet be proved or disproved unequivocally except in the case of certain rare earth activators.

It is entirely possible that the activator exists in such a distorted force field in the crystal that it has no true bonding in the sense of the "valency forces" we might assume for the atoms of the host crystal.

Hydrogen chloride

The extremely high efficiencies of samples fired in hydrogen chloride make untenable any hypothesis which demands the presence of oxide ions in the host crystal as a requisite for efficient phosphors. Because zinc chloride, as such, is not an exceptionally efficient flux (15), its formation alone cannot be responsible for high efficiencies. One possibility is that traces of "killers," such as nickel or iron, which may not have been removed during the fractional purification, were then volatilized as the chlorides. It is also to be noted that hydrogen chloride acts in the nature of a "neutral" atmosphere since it causes almost no spectral shift.

In the case of hydrogen-chloride firing of the zinc-cadmium sulfides, a loss of zinc took place because of the low boiling point of the zinc chloride formed, but it occurred uniformly throughout the charge. This loss accounts for the large shift towards longer wavelengths shown in Fig. 7. Here again, despite the loss of zinc which made the sample richer in cadmium (and hence theoretically less efficient), the cathodoluminescent efficiencies were abnormally high.

Reducing conditions

When chloride fluxes were present, firing in hydrogen sulfide was valueless because the fluxes were converted to their respective sulfides. The sodium sulfide, because of its low melting point, gave rise to fused, discolored products which were devoid of luminescence.

Firing in hydrogen was totally unsatisfactory. When fluxed samples were fired in hydrogen, the products were so sintered (they appeared as though fused) that washing of the samples was extremely difficult and sometimes impossible. It appeared that growth of zinc sulfide was such as to make the entire charge a mass of intergrown zinc sulfide crystals. Without flux this did not occur; the product remained soft, but it was almost nonluminescent. Zhirov (3) was the first to report that hydrogen causes recrystallization of zinc sulfide phosphors.

Hydrogen firing of zinc-cadmium sulfide was unsatisfactory from still another viewpoint. Here, the ease of sublimation of cadmium sulfide in hydrogen caused the product to be so inhomogeneous as to be useless.

Oxidizing conditions

The "oxide effect" in the zinc-cadmium series was even more pronounced than with zinc sulfide alone. The results summarized in Table IV indicate that the oxide effect is due, not to any selective volatilization, but to some incorporation of oxide ion. The values for the "No H_2S" column were obtained from a zinc-cadmium sulfide which probably had a small amount of oxy-anions occluded during the precipitation processes. Appreciably the same efficiencies were obtained from this sample in nitrogen whether it was fired with or without flux. When, however, it was treated with hydrogen sulfide in the manner previously described, and then fired in nitrogen

either with or without a flux, lower peak and visual efficiencies were obtained and a shift of 100 Angstroms towards shorter wavelengths was observed. A portion of the material pretreated with hydrogen sulfide was fired in the oxidizing sulfur dioxide atmosphere whereupon efficiency values and spectral distributions were obtained which almost perfectly matched the untreated material. When the untreated material was fired in sulfur dioxide, a shift of 50 Angstroms towards the longer wavelengths was detected. We may interpret these results by concluding that when the material was fired in hydrogen sulfide, oxide ions were removed and the peak shifted towards shorter wavelengths; when it was fired in an oxidizing atmosphere it was shifted towards longer wavelengths. The reduced material fired in sulfur dioxide regained substantially the same amount of oxide which had previously been removed, and hence the original values of peak efficiency and wavelength were obtained.

There is, therefore, reasonable evidence to indicate that oxide ion itself is responsible for most of these variations. Sulfate ion is ruled out, since all investigations concerned with the oxidation of zinc sulfide by oxygen or sulfur dioxide have shown that only zinc oxide is formed (16, 17, 18, 19).

TABLE IV. *Efficiencies of zinc-cadmium sulfide (47:53)*

0.01% Ag—1000°C.

Visual efficiency/peak efficiency

Atmosphere	H_2S pretreated			No H_2S		
	Efficiency, no flux	Efficiency, 2% NaCl	Peak emission (Angstroms)	Efficiency, no flux	Efficiency, 2% NaCl	Peak emission (Angstroms)
N_2	113/106	106/97	5580	120/126	120/124	5680
SO_2	126/130	123/127	5680	120/123	125/132	5730

Strong oxidation of the zinc-cadmium sulfide, such as that obtained with oxygen, causes volatilization of cadmium oxide, as Kamm (5) has reported.

The practice of covering charges with sulfur or zinc sulfide to prevent oxidation (1, 5) is undoubtedly advantageous in reducing the amount of oxidation, but if any appreciable amounts of sulfur dioxide have access to the charge, some oxidation (possibly beneficial) will occur. It is possible that traces of reducing gases, such as carbon disulfide, hydrogen, hydrogen sulfide, or carbon monoxide may be used to control the amount of oxygen reaching the charge; it is not recommended, however, that these gases be used in pure form if efficient phosphors are desired.

It is of some interest to note that moderately efficient phosphors may be obtained without the use of a chloride flux. Kamm (5) first noted this possibility in the zinc-cadmium solid solutions. The efficiency of such phosphors is considerably improved if fired in a mildly oxidizing atmosphere or if the charge originally contained the correct proportion of oxide ions. It appears that zinc sulfide flux-free phosphors may also be prepared in an efficient form if slight oxidation during firing is permitted. It is possible that any process which causes crystal growth in such a manner that the resultant crystal is under strain will form a base matrix for phosphors. This matrix may be brought about by certain fluxes (or the

product of a metathesis reaction between base and flux) which have trace solubilities in the host lattice (11), or it can be brought about, as in the case of the zinc-cadmium sulfides and, apparently, the zinc oxide-zinc sulfide compounds, simply during the formation of solid solutions.

It has long been known (8, 9, 10) that the introduction of oxide into the zinc sulfide lattice causes a shift in the emission spectrum towards longer wavelengths similar to that caused by extremely small concentrations of copper. At the present, it is premature to attempt to report the quantitative shift caused by oxide ion, but it may be said qualitatively that extremely small amounts merely broaden the long-wavelength tail (Fig. 2). As the amount is increased, the entire curve is apparently shifted symmetrically towards longer wavelengths (Fig. 5). What influences, if any, the "oxide effect" has on trap depths or other measurable properties of the phosphors is still unknown. There is little doubt, however, that the preparatory conditions of phosphors used as a basis for theoretical work should be rigorously checked and accurately described. Otherwise, the conclusions deduced from measurements of unspecified materials might be quite erroneous.

CONCLUSIONS

The cathodoluminescent efficiencies and emission spectra of silver-activated zinc sulfide phosphors and zinc-cadmium sulfide phosphors fired in a variety of gaseous atmospheres have been determined. The data show that mildly oxidizing conditions give the most efficient phosphors, while reducing gases give rise to inefficient ones. Nitrogen, and water vapor plus nitrogen, are effectively neutral atmospheres. Samples fired with hydrogen chloride showed some anomalies; the efficiencies were higher than expected but the emission spectra were not altered. Moderately efficient zinc sulfide phosphors have been prepared without a chloride flux.

ACKNOWLEDGMENTS

The author wishes to thank Messrs. A. E. Hardy and J. Wasenda for the measurements of efficiencies and emission spectra, and Messrs. J. A. Markoski and D. H. Wamsley for encouragement and advice.

Any discussion of this paper will appear in the discussion section of Volume 93 of the Transactions of this Society.

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This Is Your Journal

By means of the questionnaire of last spring and other channels, the membership of the Society has expressed itself as favoring the establishment of a monthly journal for the publication of technical papers. To meet this demand the Journal of the Electrochemical Society was designed and now makes it bow. We believe it will be a means whereby the Society can be of greater service to its members and thereby further strengthen the organization.

Each issue will contain several of the technical papers that are prepared for presentation before the Society's spring and fall meetings. In addition there will be, in a news and current affairs section, much of the same type of information that heretofore has appeared in the Bulletin. Through the new publication you will be kept informed of the actions taken by the Board of Directors and of the activities of the various divisions and committees. More space will be devoted to the news and meetings of the local sections. Publication of the technical papers monthly in the Journal will make them available in libraries throughout the world much earlier than has been possible through the Transactions. However, the Transactions will be available for those who want the discussion of these papers as well as the papers in bound form. Naturally, there will be no further distribution of the Bulletin nor preprints of technical papers.

As far as possible technical papers will be published in the order in which they are received. The monthly publication schedule provides prompt publication throughout the year. Since not all papers can be published before the meeting at which they will be presented, it behooves authors to submit their manuscripts early. This practice also will assist the editors in keeping an even flow of papers throughout the twelve issues of the year.

We need your assistance. Your suggestions for the improvement of the contents of the Journal will be appreciated. Tell us how we can serve you better. Remember this is your own journal and that we want to make it as worthwhile to you as humanly possible. Furthermore, we need your understanding and patience, understanding of our problems and difficulties, and patience with our mistakes and delays.

J. A. L.

News Notes

INFORMATION PLEASE!

The Secretary's office plans to publish sufficient material of interesting news value concerning individual members, Section and Division activities in this journal. Members are urged to advise the Editor of new professional or industrial interests and connections. It is hoped that Section and Division representatives, in addition to furnishing news of activities in their Sections and Divisions, will also contribute information concerning new developments in electrochemistry. Research directors and others supervising groups of men, and university professors directing the work of students may give valuable assistance to the journal staff by advising of changes, promotions, and industrial opportunities affecting men working with them in the electrochemical field.

DIVISION NEWS

Electrodeposition Division

Ralph Shaffer, *Secretary-Treasurer*

Cleveland Graphite Bronze Co.
Cleveland, Ohio

At a meeting of the Electrodeposition Division, during the Boston Convention, at which A. G. Gray, Vice-Chairman, presided in the absence of Chairman E. H. Lyons, the following officers were elected:

Allen G. Gray, E. I. Du Pont de Nemours & Co., Inc., Niagara Falls, New York, Chairman
Henry B. Linford, Columbia University, New York, Vice-Chairman
Ralph Shaffer, Cleveland Graphite Bronze Co., Cleveland, Ohio, Secretary-Treasurer

Following usual procedure, past officers of the division were elevated to new posts, and a nominating committee presented Dr. Ralph Shaffer's name as the new incoming officer to serve as Secretary-Treasurer. The division is very fortunate to have Dr. Shaffer working in the electrodeposition field.

The main business discussed before the division was the revision of *Modern Electroplating*. It was agreed that the revised papers should constitute material for a symposium at the 1948 New York Fall Convention. It is the chief purpose of the division to make *Modern Electroplating* the informative and dignified book on electroplating that it should be.

SECTION NEWS

Detroit Section

J. R. Heard, Jr., *Secretary-Treasurer*

Wyandotte Chemicals Corp.
Wyandotte, Michigan

Electron Microscopy in Research and Chemistry was the topic presented by Mr. William L. Grube before the Section's meeting at the Wardell Sheraton Hotel, November 21, 1947. The electron microscope has opened a new domain in microscopy and is ordinarily regarded as a tool for study of small organisms beyond the range of the optical microscope generally used in bacteriology, biology, and medicine. With it magnifications up to 100,000 are possible. Mr. Grube described its application in various branches of science and illustrated its use in industrial research with slide projection.

Mr. Grube is in the Physics Instrumentation Department, General Motors Corporation, and was born in Columbus, Ohio, 1918, receiving his B.Sc. degree in Physics from Ohio State University in 1940. An Industrial Research Fellowship at the University of Cincinnati led to an M.Sc. degree in Engineering in 1942. Since graduation, he has been employed by General Motors Corporation, Research Laboratories Division, in the Electrochemistry and Physics Instrumentation Departments. Currently his work involves the applications of electron microscopy to industrial research.

Metropolitan New York Section

Johnstone S. MacKay,
Secretary-Treasurer

1937 W. Main Street
Stamford, Conn.

The Executive Committee of the Metropolitan New York Section assembled for a dinner meeting at the Society's offices on West 102nd Street, on the evening of December 3rd, to

discuss several business matters. A. B. Kinzel, Vice President of Union Carbide & Carbon Corporation will speak on "Stainless Steel" at the next meeting of the Section, January 14, 1948.

MIDLAND SECTION

Roy C. Kirk, *Secretary-Treasurer*

Dow Chemical Co.
Midland, Mich.

The Midland Section participated in a joint meeting of the Engineering Society of Midland, the Electrochemical Society, and the American Chemical Society held on October 14, 1947, celebrating the fiftieth anniversary of the Dow Chemical Company. Dr. Willard H. Dow, president, presided at the meeting and T. H. Griswold outlined the history of the company, paying tribute to its founder, the late Dr. Herbert H. Dow. Ralph M. Hunter spoke on the history of the electrochemical industry in this country for the past fifty years and outlined the development of the electrolytic cell which has been a factor in making Dow the world's largest producer of chlorine. Magnesium, also a product of Dow's electrochemical industry, was also discussed. This discourse appears later in this issue. Dr. E. O. Barstow, who joined the company in 1900, outlined the utilization of Midland brine for the production of inorganic chemicals, including bromine, chlorine, caustic soda, calcium chloride, magnesium chloride, and epsom salts.

The Section also held its President's Day dinner meeting in honor of Chairmen of the Midland Section on November 10, 1947, at the Midland Country Club. R. I. Thrune, Chairman, W. S. Loose, past Chairman, R. C. Kirk, and H. A. Robinson presented interesting talks on the Boston Convention. R. M. Hunter's discussion of "The Organization of the Electrochemical Society on a National Level" highlighted the occasion. R. D. Blue, past Chairman, gave an entertaining talk on "Reminiscing." The meeting was very well attended and a lively informal discussion period ended the program.

PERSONALS

Edward B. Sanigar has been appointed a member of the Publication Committee representating the Theoretical Electrochemistry Division. His present address is Radiation Laboratory, San Francisco Naval Shipyard, San Francisco 24, California.

Hugo A. Barbian, formerly research metallurgist, The Dow Chemical Company, Midland, Michigan, is now employed at the Western Cartridge Company, Division of Olin Industries, Inc., East Alton, Illinois.

Mars G. Fontana, Ohio State University, is one of the recipients of a grant-in-aid from the Research Corporation, New York, it has been announced. The Frederick Gardner Cottrell Fund for grants-in-aid of postwar science, established by the Research Corporation, has announced that more than 100 grants were approved in 1946. Dr. Fontana's work, under one of the grants in the field of chemistry and chemical engineering, is on improved methods of corrosion testing with special reference to erosion-corrosion.

Robert G. Seyl announces the establishment of the SEYL Laboratories, consultants on corrosion, with offices in Chicago, Illinois.

William B. Price, Director of Research, Scovill Manufacturing Company, Waterbury, Connecticut, has announced his retirement from that company effective January 1, 1948.

Dr. Allen G. Gray has succeeded Dr. Ernest H. Lyons, Jr., as Chairman of the Electrodeposition Division for the year 1947–1948.

Carsten Steffens, formerly Assistant Research Director, General Printing Ink Corporation, New York, is now Director of Chemistry, Stanford Research Institute, Stanford, California.

MEET THE STAFF

In direct charge of the Secretarial Office is John W. Cornwell, Assistant Secretary and Managing Editor, appointed by and responsible to the Board of Directors but under the supervision of the Secretary. Reporting to Mr. Cornwell are Misses Virginia Mergenthaler and Audrey Skvarla engaged in secretarial and business operations, and Miss Gladys Garland, Assistant Editor, whose duties are apparent.

POSITIONS AVAILABLE

CHEMIST for research position needed by nationally known producer of chem-

icals in Detroit area. Experience in metal cleaning and finishing, and electroplating required. Include full details of education and experience and state salary requirement in first letter. Reply to Box A-193, Electrochemical Society, Inc., 235 West 102nd St., New York 25, N. Y.

ASSISTANT PROFESSOR OF ELECTROCHEMISTRY: Technical institute in Chicago requires a man with good background in electrochemistry and associated phases of physical chemistry for permanent teaching staff. Applicants should have demonstrated ability to carry on independent research. Salary for nine months school year is $3600, with additional stipend for summer teaching if and when such work is available. Reply to Box A-194, Electrochemical Society, Inc., 235 West 102nd St., New York 25, N. Y.

RESEARCH CHEMIST FOR ELECTROPLATING. Must have good background and experience for developing plating processes. Prefer young man who is interested in a future with an old established progressive firm. Location Chicago. Reply to Box A-195, Electrochemical Society, Inc., 235 West 102nd St., New York 25, N. Y.

GRADUATE ASSISTANTS: Several assistants needed for teaching or research in ELECTROCHEMISTRY by technical institute in Chicago. Half of the full graduate study load per semester is permitted for Ph.D. or M.S. candidates. Stipend is $1275 for nine months, with additional compensation for summer work. Reply to Box A-196, Electrochemical Society, Inc., 235 West 102nd St., New York 25, N. Y.

GRADUATE STUDENT IN METALLURGY (brass) familiar with x-ray spectra and electron microscopy. Preferably located in Chicago district. Reply to Box A-197, Electrochemical Society, Inc., 235 West 102nd St., New York 25, N. Y.

PHYSICAL AND ELECTROCHEMISTS FOR RESEARCH. Training or experience in electrolysis of metals in fused salts will be of value. Excellent opportunity in laboratory located in New Jersey. Submit qualifications and salary expected. Reply to Box A-198, Electrochemical Society, 235 W. 102d St., New York 25, N. Y.

POSITIONS WANTED

ELECTRO AND METALLURGICAL CHEMIST: B.S. and M.S. degrees, age 42. Experienced in: Corrosion; electroplating anodizing, electropolishing, cleaning, pickling, and other phases of metal finishing; fused salts; electrochemical analysis; electrophoresis; organic and inorganic electrochemical preparations. Desires responsible executive position. Reply to Box 315, Electrochemical Society, Inc., 235 West 102nd St., New York 25, N. Y.

ELECTROCHEMIST: B.Sc., Ph.D. (London) desires position in America as consultant and/or technical adviser for research and development divisions of electrochemical and chemical process industries. Author of technical publications, including brass plating processes, bonding of rubber to metals. Fluent knowledge of French, German and Roumanian. Nine years industrial experience. Age 35; married; residing in London. Reply to Box 316, Electrochemical Society, Inc., 235 West 102d St., New York 25, N. Y.

FIFTY YEARS OF ELECTROCHEMICAL HISTORY

R. M. HUNTER

To fully appreciate the significance of fifty years of electrochemical manufacturing in The Dow Chemical Company it is desirable to consider the accomplishments of the Company in the American electrochemical industry. Herbert H. Dow received conspicuous recognition of achievements in science, the award of the Perkin Medal in 1930, citing five types of chemical endeavor, four of which were electrochemical. His first manufacturing efforts were primarily electrochemical and the Company which he founded is one of the electrochemical industries of the world.

Sixty-five years before 1897—the year Herbert H. Dow founded the Dow Chemical Company in Midland—the invention of the Voltaic Pile enabled Sir Humphrey Davey and his brilliant assistant Michael Faraday to embark upon a series of experiments which nailed down the fundamental laws of electrochemistry. Later English and German scientists continued the work so that by 1885 considerable literature had developed, based upon the laboratory use of the Pile and the primary cells. Commercial exploitation was impossible with such sources of power. Fortunately at this time, the dynamo electric machine was invented and Edison, Westinghouse, and others gave the world the tools for the electric age.

While the electrical engineers were arguing the relative merits of AC and DC, a galaxy of young chemists appeared upon the scene who did not participate in the electrical engineers arguments but continually demanded of them larger machinery with which to carry out their manufacturing processes.

I have used the expression "young chemists" advisedly; many of them did their basic work when in college and were captains of the industries while in their early thirties. If growth is a measure of success, their efforts were successful.

RALPH M. HUNTER

Taken as a whole, the American electrochemical industry doubles its consumption of electric power every six years and in 1943 it was consuming at the rate of 7,000,000 KW, which was 20% of all the electric power produced in the United States.

What was the state of this industry in 1897? Ten years before Charles Hall, in the barn of his home in Oberlin, Ohio, invented a process for the production of aluminum which was competitive with the existing processes. In 1897 the aluminum industry, at the insistence of Arthur Vining Davis, a night operator, whose fame is perpetuated by Arvida, Quebec, moved to Niagara Falls to get more power. The electrolytic aluminum industry is healthy, it doubles its capacity every six years.

In 1897 Edward G. Acheson, who had founded the Carborundum Company and lost it through financial misfortune, was then embarking upon the manufacture of graphite. In the conduct of the affairs of the graphite business, he did not duplicate his mistake in carborundum. The graphite industry has grown. Carborundum, under the guidance of Frank Tone, is the largest of the artificial abrasives, an industry which doubles its production every six and a half years.

In 1895, Wilson and his associates reduced lime with coke in the electric arc and produced metallic calcium which they sent to France for evaluation. It took a long time before they learned that their calcium was in reality calcium carbide which had no value except for the production of acetylene. "Carbide" Wilson, as he was then always known, may rest secure in the knowledge that after fifty years nobody reproaches him for his failure to make calcium. The development of carbide was carried on by Frederick Becket, a brilliant researcher in the electrothermal field, whose work led to the electrometallurgical production[4] of ferro alloys. Ferrosilicon is a typical one, the production of which doubles every seven years.

In 1890, Ernest LeSueur working one summer while still a student at M.I.T., patented an electrolytic diaphragm cell for the production of alkali chlorine, which by 1893 was successfully operating in Rumford Falls, Maine. The same plant with the originally designed equipment is still operating.

In 1897, H. Y. Castner was developing and installing mercury cathode cells in Niagara Falls for the Mathieson Alkali Works. Their general type is still in operation by the same company and until 1938 were the principal mercury cells in America. Castner, disappointed in the acceptance of his idea in America, went to Europe and was quite well received in England.

In 1892, five years before, Herbert H. Dow was credited with having produced bromine electrochemically and in 1896 with the production of bleaching powder from electrolytic chlorine. Today chlorine is recognized as an index of the chemical industry, having displaced sulphuric acid. Chlorine's coproduct, electrolytic caustic soda, has always been a hindrance rather than a help because ammonia soda caustic was a product of a highly engineered and successful

industry and was of a quality difficult to equal.

In 1909, the first car of liquid chlorine was shipped by Pennsylvania Salt and the death knell of bleaching powder was sounded, but as Mr. Strosacker has pointed out, long before that the Dow Company had begun to forsake the path of electrochemistry alone and had wed the odorous but highly solvent organic chemical industry, so that in 1915 when bleaching powder was discontinued, The Dow Company had taken a course divergent from that of other electrolytic alkali chlorine producing companies.

As Mr. T. H. Griswold has pointed out, the trap type bromine and chlorine cells did not make caustic soda. By 1912 it was obvious that chlorine could not alone carry the cost of electric power, and that the diaphragm cell, which manufactured chlorine and 8% caustic soda, was necessary, and so in 1914 the trap type was discarded in favor of the D. G. diaphragm cell. This cell was hard to handle, but had a great influence on the present cell design of The Dow Company.

In the electrolysis of strong sodium chloride solutions, as the electrolysis proceeds, NaCl is consumed faster than water and the concentration of chloride ions is reduced. If electrolysis continued indefinitely, water would result and the cell would be making O_2 or CO_2 since only OH ions would be present to be discharged at the anode.

The mercury cell avoids this by removing the brine solution when it is only 10% decomposed, resaturating it and returning it.

The diaphragm cell attempts to overcome it by permitting the salt solution to percolate through the diaphragm from anode to cathode when the salt solution is about half decomposed. Unfortunately, the problem is not solved so easily. The fact that caustic soda accumulates at the cathode as the result of hydrogen discharge, places an all too large source of OH ions close to the diaphragm. During electrolysis OH ions migrate toward the anode chamber in quantity, since they carry a negative charge. However, the percolating anode liquor should theoretically balance the speed of OH ion migration and prevent it from progressing beyond a point somewhere within the diaphragm. This requires a uniform diaphragm, otherwise, the cell is inefficient and graphite is consumed excessively.

To jump immediately to the present it may be of interest to you that to produce caustic soda at 120 g/L, which is roughly the product of 50% decomposition, requires that each sq. in. of diaphragm pass uniformly three drops of solution per minute. An orifice of less than 0.01 of an inch will pass more than this amount. Therefore, it is the problem of diaphragm design to see that a large number of very small pores uniformly pass three drops per minute for each sq. in. of the twelve and a half acres of asbestos diaphragms which are right now percolating in the plants of The Dow Chemical Company.

The D. G. diaphragm cell had a thick diaphragm of cement and asbestos paper. The electrical resistance was high and the percolation was so low that the decomposition of salt was far in excess of the 50% now considered good. The current efficiency was low and the cell experienced the difficulty of frequent unpredictable diaphragm failures. It consisted of seventy-five units clamped together in filter press form and was made of cement, thus it resembled our present cell. With all its faults, it permitted the production of twenty-five tons of chlorine per day during the first World War even if it did require an operating and maintenance personnel of about 300 men.

In 1920 it was succeeded by the Method 21 cell, which employed a thin asbestos paper diaphragm with ample percolation. The cell body was cast in the same forms used for its predecessor, the D. G. cell, and it was erected in the same buildings and on the same skids. It employed eighty-five units instead of seventy-five since its resistance was lower and it operated at a thousand amperes in contrast to the 600 amperes of its predecessor. The filter press arrangement on the skid has remained a Dow tradition.

The electrical circuit resistance has always been low and construction costs are low. It retained heat, thereby, further lowering electrical resistance and no competitive cell has ever equaled its efficient use of floor space.

The Method 21 cell had a profound effect on tradition. The Dow bromine cell consumed about four volts with a fair current efficiency. If chlorine could be produced in the Method 21 cell with its coproduct caustic soda for the same power as that required for the production of bromine alone, it was obvious that the electrolytic production of bromine should be abandoned and its

liberation accomplished by the use of chlorine. So about 1920 we find the bromine traps discarded and a chlorinating tower substituted.

Comparison of the Method 21 cell with the efforts of H. K. Moore, at The Brown Co., L. D. Vorce, a classmate of H. H. Dow, at Pennsylvania Salt, and Frank Wheeler, at Kimberley-Clark, were favorable to M-21. The M-21 cell enabled The Dow Company to grow from 25 tons/day to 200 tons/day an expansion which was carried out in three buildings within our factory. In 1938, the company began to expand by the acquisition of the Great Western Division, and shortly thereafter the production of chlorine in Texas followed. This was accomplished by a new type of cell called the M-25. This cell was largely a redesign of the M-21 which permitted us to increase the current to 10,000 amperes and produce five times the chlorine within the same space. When this design came into the competitive field it was not challenged by the round Vorce cell, which was predominate up to 1935, but rather by the Hooker Company Stewart cell which has enjoyed great popularity from 1939 to the present. The Velasco Magnesium Plant which The Dow Company recently purchased from the United States Government contains Hooker cells which have operated successfully for four years. The expansion now going on at Velasco is being carried out by Method 25 Dow filter press cells.

The American chlorine industry despite its uphill fight with electrolytic NaOH has enjoyed a healthy growth. In the early 1940's the production of electrolytic NaOH exceeded that of chemical NaOH which has a slow growth rate of doubling in thirteen years. This was to be expected for the electrochemical chlorine industry of the United States doubles every six and a half years.

The Dow Company has not been content with six and a half years to double production, it now accomplishes this growth in five years. In 1923, Dow was producing about 8% of American chlorine and was exceeded in volume by several companies. Today it is unquestionably the largest producer of chlorine in the world and account for 28% of the American production. A growth of doubling production every five years is the fastest rate that I have quoted to you.

The story of magnesium does not need to be retold but it is a big part of our fifty years of electrochemistry. It was a "natural" for The Dow Company since it produced $MgCl_2$ and always had uses for chlorine. In the summer of 1916, a bar of magnesium was produced here; production had started, but all did not go well.

A potline of thirty cells of 3,000 amperes capable of producing 1800 pounds per day failed after a few days of operation in 1917. Its more modest successor which was producing slightly less than 1000 pounds per day burned in February, 1920, in a very spectacular fire.

By 1923, six cells were operating at 3,000 amperes, and the plant production was about 300 pounds per day. The next six years were marked by investigations of the proper type of feed. Anhydrous magnesium chloride, produced by drying in hydrochloric acid, was the most attractive form although magnesium chloride, produced by the decomposition of the double salt of ammonium chloride magnesium chloride, was also investigated. An extensive experiment on the use of anhydrous carnolyte, a mixture of potassium chloride and magnesium chloride, was not successful, but the possibility of the use of magnesium chloride—$1\frac{1}{2}$-$2H_2O$ was tried and gave good results despite the fact that the efficiency was lower and the graphite consumption was higher. It also became evident that whether we liked it or not, the cell bath was going to consist of sodium chloride and calcium chloride in the proportions to which they existed in the cell feed as impurities, and that we might as well learn to live with them.

In 1927, experiments on a larger cell were inaugurated because the plant had expanded from six cells to thirty cells at 3,000 amperes. By that time the magnesium growth curve had been established. From 1920 to 1939 magnesium production doubled every two and a half years.

A plant consisting of sixteen cells at 15,000 amperes was built in 1929. The cells were rectangular instead of round, had sixteen anodes instead of one, and resembled the present day cell. It was rated at about 250 pounds per day and it was far from perfect. It had barely gotten into operation when a group of French electrochemists inspected it for the purpose of deciding their policy in France and to quote them "those were heroic days". They decided that the Germans were somewhat ahead of us

for they purchased 1G cells. From 1930 to 1937 we enjoyed a period of excellent development conditions. It was during this time that the cell grew from 15,000 amperes to 55,000 amperes with very slight increase in setting size and as the demand increased we merely put in another motor generator set and increased the rating of the cell.

The argument of anhydrous feed versus $1\frac{1}{2}H_2O$ feed was resolved overwhelmingly in favor of the wet material and its accompanying high graphite consumption of 0.1 lb. graphite per pound of metal. To meet this demand a plant for the production of magnesium cell electrodes was erected making the Dow production program independent of raw materials.

So it was that in 1939 when production was tripled in Midland and the Texas gulf plant was started, magnesium was ready to move. In fact this expansion was good experience for the eruption of production which followed, for when the smoke cleared away in 1943, the sixteen cells of 1937 had increased to nearly 800.

The Marshall brine which was used by Dow for the first forty-seven years of its existence was unique in that it contained no potash, sulfate, boron, or ammonia. From time to time we heard of difficulties other alkali chlorine producers had due to ammonia and sulfates. After experimenting with carnolyte in the 1920's and the experience with boron when we moved to Texas, the absence of potassium and boron is considered a blessing. I sometimes wondered if Dr. H. H. Dow was fortunate in locating in Midland and operating on the Marshall brine and that if the Company's progress would have been impeded in another location. Expansion beyond and changing conditions within the home town have made it necessary to use these objectionable impurities and the difficulties have all been overcome. We recognize the inevitable success of sound engineering, research, diligence, ambition, and the American system of business.

NEW MEMBERS

At the meeting of the Executive Committee held on December 5, 1947, at the office of the Electrochemical Society, Inc., 235 West 162nd St., New York City, the following were elected to membership

Harold G. Bell, West Virginia Pulp and Paper Co.; mailing add.: Box 26, Covington, Va. (Theoret. Electrochemistry, Alkali and Chlorine)

Herman Ebbinge, N. V. Hollandsche Metallurgische Bedrijvin; mailing add.: Lyceumplein 19, The Hague (Theoret. Electrochem., Electrodeposition, Electrothermics)

Charles R. Fisher, National Carbon Co., 230 N. Michigan Blvd., Chicago, Ill. (Batteries)

Wilber G. Hespenheide, Battelle Memorial Institute, 505 King Ave., Columbus 1, Ohio (Theoret. Electrochem., Organic Electrochem., Electrodeposition)

George C. Kuczynski, Sylvania Electric Prod., Inc., Sylvania Center, Bayside, L. I. (Theoret. Electrochem., Corrosion)

David Linden, Signal Corps. Engineering Labs., Fort Monmouth; mailing add.: 39 Madison Ave., Long Branch, N. J. (Batteries)

John V. McCandlish, Bar-Rusto Plating Corp., 1810 Locust St., Kansas City, Missouri (Corrosion, Electrodeposition)

Ernest Charles Mills, High Duty Alloys Ltd.; mailing add.: Southmead, Farnham Common, Bucks, England (Corrosion, Electrodeposition)

H. Bernard Schoch, P. R. Mallory and Co., Inc.; mailing add.: 1026 N. Garfield Dr., Indianapolis 3, Indiana (Organic Electrochem., Batteries, Corrosion, Electrodep., Electronics, Dielectrics)

Meyer Steinberg, Deutsch and Loonam, mailing add.: 23-09 Astoria Ave., L. I. C. 2, N. Y. (Theoret. Electrochem., Electrodeposition)

Frank Anthony Ticulka, Armour Research Foundation; mailing add.: 3210 W. 64 Pl., Chicago 26, Illinois (Electrodeposition, Electronics)

Lynn D. Wilson, Corn Products Refining Co., mailing add.: 3322 W. 61st Pl., Chicago 29, Illinois (Theoretical Electrochem., Electrodep., Dielectrics)

Charles Henry Winter, Jr., E. I. du Pont Co., mailing add.: 301 S. Gray Ave, Wilmington, Del. (Theoret. Electrochem., Electrodep., Electrothermics, Electronics)

Frank Alfa Young, Susquehanna Pipe Line Co., 1608 Walnut St., Phila. 3, Pa. (Theoret. Electrochem., Batteries, Corrosion, Electronics)

The Enthusiasm of Youth

It was a group of comparatively young men who met in Philadelphia on April 3, 1902, to organize the *American Electrochemical Society* and who received congratulatory messages from Van't Hoff and Haber on behalf of the *Deutsche Electrochemische Gesellschaft*, and who were in turn to welcome the organization of the *Faraday Society* a few months later. In their thirties and early forties, the moving spirits in founding our Society were inspired by visions of the future potentialities of that recently recognized branch of science and technology called "electrochemistry." In the decade that followed they developed a vigorous forum for the exposition of electrochemical theory and practice. There can be no question that the Society of those early years contributed much to scientific achievement and even more to the development of electrochemical industry.

It is fair to ask why the size and influence of the Society has not kept pace with the remarkable growth of electrochemistry. A measure of this growth may be seen in the increase in power consumption by the electroprocess industries which in 1943 was about 60 billion kw-hrs. or three times the total electric power generated in the entire United States in the year 1913. Yet the Society remained more or less static during this period.

It is to be suspected that the principal reason The Electrochemical Society has not realized its early promise lies in the failure to bring more young men into participation in its activities and into management of its affairs. This is evidently the view of the majority of the present membership who responded to the questionnaire of last April, the results of which are summarized elsewhere in this issue. "Younger blood is needed in official capacity" seems to be the consensus of these replies. Recognition of this conclusion is implied in many steps already taken. Emphasis has been placed upon divisional activities and the chairmen of Divisions have been made members of the Board of Directors. The Publication Committee has been reorganized in a way to put more responsibility for the quality of technical papers upon Division representatives. Local Sections have been given more financial support and steps taken toward organizing these groups and giving them representation in the Board. There has long been a Young Author's prize; there is the Weston Fellowship; grants-in-aid from the Roeber Research Fund so generously founded by the Secretary Emeritus. Much has been done, but much more remains to be done if the Society is to benefit fully from the enthusiasm, inspiration, and energy of youth.

R. M. B.

News Notes

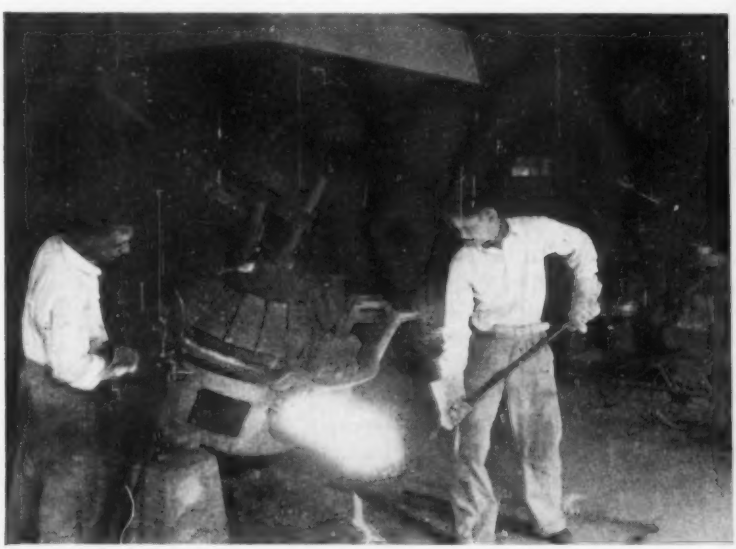
INDUSTRIAL COLUMBUS

It is an accepted fact that each city has its own individual advantages to offer industry. Columbus has one great advantage which has been a dominant factor in its development—that of geographical location. It is strategically situated between coal and iron deposits and within easy reach of other raw material supplies. The city's location in the heart of a thriving agricultural region has combined with its political and educational status to round out a well-balanced community.

In the industrial sphere, Columbus maintains this balance through a diversity of manufacture which precludes domination by any single industry. There are approximately 700 manufacturing establishments in Columbus representing wide industrial variety. The Jeffrey Manufacturing Company, for example, is a manufacturer of mining, material handling, and processing equipment and has served the needs of practically every known industry since 1877. It is a worldwide institution with many district offices in the United States, and plants in Canada, England, and South Africa, in addition to its local plants. The Curtiss-Wright Corporation plant in Columbus has made an enviable record in the aircraft industry and is the headquarters for the airplane division of the corporation. It is currently engaged in considerable overhaul work and the manufacture of experimental as well as commercial planes.

The Fisher Body Co., Ternstedt Division, has recently opened what is probably the city's most modern plant which is engaged in the manufacture of automobile parts. The finishing department of the plant includes considerable painting and electroplating work.

Other manufacturing in Columbus, includes: roller bearings, hydraulic equipment, coated fabrics, glass products, railroad cars, steel castings, and many others. Numerous smaller industries, established as a result of the community's war experience, are remaining in Columbus for peacetime operations.



Pouring metal from the electric arc furnace at the Engineering Experiment Station, Ohio State University

SECTION NEWS

Cleveland Section

C. B. Sanborn, *Secretary-Treasurer*
2231 Wrenford Road
University Heights 18, Ohio

The first meeting of the Cleveland Section for the 1947–48 season was held at the Hotel Carter on October 21, 1947. Dr. A. L. Ferguson of the University of Michigan spoke on "A Summary of the Researches on Polarization and Overvoltage at the University of Michigan." Dr. Ferguson spoke before the Cleveland Section last year and the marked interest in the subject prompted the program committee to invite Dr. Ferguson to present the results of his latest investigations again this year. Details of additional data obtained on the relation of concentration to overvoltage and polarization, decomposition potentials, and residual currents were explained in a highly illustrated lecture. Dr. Ferguson described polarization and overvoltage as active potentials having nothing to do with IR drop. His data graphically demonstrated that overvoltage is a function of current density. In closing Dr. Ferguson discussed the relation of polarization and overvoltage to practical problems of polarographic analysis, electrodeposition, etc.

Mr. L. F. Oeming, Sanitary Engineer, Michigan Stream Control Commission, discussed "Cyanide Waste Disposal" at a joint meeting of the Cleveland Section and the Electroplaters Society on November 11, 1947, at the Hotel Carter. In opening his discussion on this subject, Mr. Oeming gave a brief history of waste disposal problems. He noted the effect of increasing size and number of electroplating concerns on streams and waterways in Michigan and throughout the country. The destruction of fish due to cyanide pollution and the menace to water supplies generally were stressed. He pointed out that plating wastes upset the sewage treatment process when the sewage plant receives them in large quantities. Also in small town areas the natural purification of streams is affected by the addition of raw wastes which are not put through a disposal plant. Even though small concentrations are passed to the stream, copper and other metal ions have an accumulative effect. Emphasis was placed on control measures. The hazardous results of treating cyanides with sulfuric acid were mentioned. Other methods such as the lime sulfur treatment, chlorination, or treatment with chlorite at pH above 8.5 were mentioned as the common or standard cyanide waste treatments.

Mr. Oeming made the following recommendations concerning the problem:

1. Full appreciation by management and personnel of problems and hazards of cyanide waste disposal.
2. Proper attention to layout of plant, sewage system, receiving water, etc.
3. Reduction of loss by drag-out and drip.

Dr. C. L. Faust, Local Chairman, Columbus Convention

4. Prohibition of direct dumping of concentrated wastes.
5. Avoid complicated disposal systems, on basis that operators tend to take hazardous alternatives.
6. Good disposal equipment and good maintenance.
7. Separate sewers for disposal, including drains in plating tanks to the separate systems.
8. Suitable pollution standard; specific standards in any locality being dependent on local conditions, stream usage, etc. Municipal systems using biological methods of sewage treatment should not accept measurable concentrations of cyanide; even the sludges from disposal treatments often over-tax municipal systems. Not more than 0.1 p.p.m. as HCN should be tolerated; 0.3 p.p.m. kills fish in a few minutes to 2 hrs., higher concentrations almost instantly. Cattle killing: per-

missible limits are higher than for fish, fish standards therefore govern.

9. Continued work on new disposal processes.

Dr. G. E. Barnes of Case Institute of Technology pointed out in the discussion period that followed that disposal of industrial plating wastes is a relatively new problem. About ten years ago expanding operations began to overtax available dilution sources thus another problem in the field of sewage treatment became the concern of sanitary engineers. Dr. Barnes also stressed the complicated nature of the wastes, pointing out, for example, that not only cyanide but also toxic metals always present must be treated in the disposal of cyanide wastes. He then briefly reviewed the work of several years which has led to the development of the 100,000 gal. per day disposal plant of Talon, Inc., Meadville, Pa., recently described in "Water and Sewage Works" **94**:(8) 1947.

The Cleveland Section met again with the Electroplaters Society on December 5, 1947, at the Hotel Cleveland to hear Mr. Myron Ceresa of Westinghouse Electric Corporation discuss "Periodic Reverse Plating." Periodic reverse plating refers to a method in which the polarity of the current through short cycles is periodically reversed. The time of the reverse cycle is much shorter than the plating cycle, the time of the reverse cycle depends on the nature and type of plating being done. By means of illustrations, Mr. Ceresa showed that with this method finer grain structures are obtained. Plating solutions, usually the alkali cyanides, operate at greatly improved efficiencies by means of periodic reverse plating. Periodic reverse plating also permits, in most cases, the utilization of much higher current densities producing tightly adherent, smooth, ductile deposits with improved corrosion characteristics.

Dr. George W. Heise, National Society President, spoke before the Cleveland Section on January 13, 1948, on the topic "Some Applications of Gas-Depolarized Electrodes." A detailed account of his presentation will appear in the March issue of the Journal.

Calendar of future monthly meetings of the Cleveland Section follows:

Feb. 10, 1948—Electrometallurgy—exact subject and speaker to be announced.

Mar. 9, 1948—Dr. Sherlock Swann, University of Illinois, "Electro-Organic Chemistry."

Apr. 13, 1948—Field trip to Goodrich Brecksville Laboratories.

May 18, 1948—Ladies night at the Fairview Community Center.

Detroit Section

J. R. Heard, Jr., *Secretary-Treasurer*
Wyandotte Chemicals Corp.
Wyandotte, Mich.

An outline of the November 21, 1947, meeting of the Detroit Section at which Dr. William L. Grube of the Research Laboratories, General Motors Corporation, spoke on the Electron Microscope appeared in the January issue of the Journal. Dr. Grube was assisted by Mr. Irwin of General Motors Corporation in demonstrating by slide projection the principles and scope of use of the electron microscope compared with that of the ordinary optical lens microscope. Several parts of the electron microscope were exhibited with emphasis on explanation of mounting of specimens for examination. The ultra-high magnification instrument is particularly valuable in studies of metallic surface coatings, extremely small particle size measurements, and the viruses causing diseases in man and animals. This was a very interesting meeting.

Dr. Jesse E. Stareck, United Chromium, Inc., spoke at the January 16, 1948, meeting at the Wardell Sheraton Hotel, choosing as his topic "Electro-Color and Pattern Plating." A summary of his talk will appear in the March issue of the Journal.

Calendar of future monthly meetings of the Detroit Section follows:

Feb. 20, 1948—John D. Piper, Research Laboratories, Detroit Edison Co., "Insulation Problems."

Mar. 19, 1948—Dr. Henry Brown, The Udylite Corp., "Porosity in Electrodeposits."

Apr. 16, 1948—Harold A. Strickland, The Budd Co., "Induction and Dielectric Heating."

May 21, 1948—Ralph M. Hunter, Supperintendent, Electrochemical Division, The Dow Chemical Co., "Magnesium Production."

Metropolitan New York Section

J. S. MacKay, *Secretary-Treasurer*
1937 W. Main Street
Stamford, Conn.

A. B. Kinzel, Vice President of Union Carbide and Carbon Corporation, de-

livered a talk before the section at its last bimonthly meeting at the Hotel Pennsylvania, January 14, 1948. His subject, "Stainless Steel," covered the history of the development, technical problems, and evolution of types of stainless steel. Mr. Kinzel discussed the resistance of types to certain media, their high temperature properties, and the evolution, from stainless steel, of high temperature alloys not normally stainless.

At the next meeting of the Metropolitan Section, Dr. Henry R. Copson of International Nickel Company will present a talk on the general topic of "Corrosion". The date for this event is March 10, 1948.

Philadelphia Section

J. F. Hazel, *Secretary*
Harrison Laboratory of Chemistry
34th and Spruce Streets
Philadelphia 4, Pa.

The Executive Committee of the Philadelphia Section met on December 17, 1947, at the Engineers' Club. In addition to Ernest G. Enck, Local Committee Chairman for the Philadelphia National Society Convention, April 13-16, 1949, the following committee chairmen were appointed:

Hotel Reservations Committee, Russell P. Heuer, *Chairman*. (The Benjamin Franklin Hotel was suggested as the Convention headquarters.)
Meeting Accommodations Committee, John F. Gall, *Chairman*
Registration Committee, Edgar L. Eckfeldt, *Chairman*
Finance Committee, Hiram S. Lukens, *Chairman*
Entertainment Committee, Harry A. Alsentzer, *Chairman*
Plant Visits Committee, Milton Barba, *Chairman*
Publicity Committee, Albert Ware, *Chairman*

In accordance with procedure suggested at the Boston Convention, it was decided that the Secretary should distribute the current program of Section meetings to the secretaries of each of the local sections, as well as an outline of the 1946-47 program with an appraisal of the speakers. February 4, 1948, is the tentative date for the next Executive Committee meeting.

Dr. George A. Perley of Leeds & Northrup Company spoke before the Section on January 8, 1948, on "Trends in the Development of Glass Electrodes." An account of this meeting will appear in a later issue of the Journal. Calendar of future bimonthly meetings of the Philadelphia Section follows:

Mar. 4, 1948—Dr. George W. Heise, National Society President, "Applications of Porous Electrodes"
May 15, 1948—Dr. Colin G. Fink will speak at the Ladies' Day meeting at Bryn Mawr.

LETTERS TO THE EDITOR

The columns of the Journal are available to readers and members of the Society for the publication of "Letters to the Editor". This provides a forum for expression of opinion or announcement of new developments in science or technology. Communications received toward the close of the month can appear within six weeks.

CATHODIC PROTECTION SYMPOSIUM AT PITTSBURGH

The papers presented at the Cathodic Protection Symposium held in Pittsburgh, Pa., the second week in December, 1947, will be edited and published by a source outside of this Society. The date at which these papers will be available will be announced in a later issue of the Journal.

NATIONAL ASSOCIATION OF CORROSION ENGINEERS

St. Louis Convention,

April 5-8, 1948

St. Louis will be host to the N.A.C.E. for their Convention to be held at the Jefferson Hotel, April 5 to 8, inclusive. The technical sessions will include symposia on: Cathodic Protection, Chemical Industry, General Industry, Oil Industry, Protective Coatings for Metals, Salt Water Corrosion, and Water Industry. Professor Mars G. Fontana, Ohio State University, is chairman of the Technical Program Committee for these sessions, and he is also a member of the National Association of Corrosion Engineers Board of Directors.

REVIEWING OF PAPERS BY PUBLICATION COMMITTEE

O. W. STOREY

A change has been effected during the past year in the procedure for the reviewing of papers submitted for publication by the Society in an effort to do both a better and quicker reviewing job and to better the quality of the accepted papers. Under the revised system the reviewing is the primary job of the several Divisions of the Society in contrast to the previous practice under which the Chairman of the Publication Committee was largely responsible both for the reviewing (though done by others) and the quality of the accepted papers.

Article V (containing 18 Sections) of the By-Laws of the Society is entitled "Publication Committee". It specifies the method of selecting the Publication Committee and defines its functions. Each Division is entitled to a representative on it. Under Section 3 that Committee "shall have charge of the publication of the Transactions of the Society and shall decide what papers shall be published in the Transactions." Section 6 further provides that: "In general, no paper may be presented at a general meeting of the Society unless it has been submitted in full prior to a date set by the Board of Directors early enough to allow consideration by the Publication Committee". This date may be changed by the Board of Directors. Other Sections set forth a general set of rules for acceptable papers.

Divisional Representatives

Under the new arrangement, the divisional representatives on the Publication Committee play an important part in the reviewing and acceptance of manuscripts submitted to the Society. They are primarily responsible for the acceptance or rejection of papers and, therefore, for the quality of those that are accepted. The divisional representatives, therefore, should have the qualifications required to do this job properly. Also, they should have the necessary time and facilities to do the job.

Reviewing Procedure

Each manuscript (three copies required) submitted to the Society is received first by the Secretary, who acknowledges receipt and enters it in the records. He also advises the author of the publication rules and requests the author to state whether the paper or its subject matter has been or is being published elsewhere. He then forwards the manuscript to the proper divisional representative, at the same time notifying the Publication Committee Chairman and the Divisional Chairman. Each Divisional Chairman therefore is kept informed about papers submitted that relate to the work of his Division.

The divisional representative assigns the paper to reviewers of his selection. He may be one himself but generally he is not a primary reviewer. The reviewers are selected from qualified members, not necessarily members of the Division to which the paper is assigned. They are selected so that the paper is reviewed from several points-of-view, for example, the practical and academic. The reviewers are guided by the following general provisions of the By-Laws:

Section 8. Papers of the following classes will be regarded as undesirable:

(1) Those containing too little information or obviously incorrect information.

(2) Those containing only information already easily accessible.

(3) Those of an advertising nature not counterbalanced by adequate scientific information and treatment.

Section 9. Authors' abstracts of papers already published elsewhere may be accepted for the purpose of discussion. Papers already published but not easily accessible will, if otherwise desirable, generally be accepted.

Section 10. In case of papers of a general or review nature solicited for a symposium, the Publication Committee may accept such papers which, in the opinion of the Board, are desirable for the complete treatment of the symposium subject.

Section 11. Concerning the question of papers dealing with analytical methods, the paper must

(1) Describe an electrochemical method of analysis or deal with analysis of a substance which enters into or is a product of an electrochemical or electrothermal process.

(2) Cover some novel method or methods or critical comparison of existing methods.

(3) Contain some actual experimental results illustrating the method.

There has been considerable difference of opinion in interpreting the phrase "not easily accessible" in Section 9 as applied to previously published papers. It is not possible to lay down any hard and fast rules and each case has to be judged individually. The Publication Committee's decisions in such doubtful cases, particularly where the paper is approved for publication, cannot and do not meet with the approval of the entire membership.

Each reviewer is requested to answer the following general questions about the papers he reviews and, furthermore, he is asked to particularize in his answers:

1. Whether the manuscript covers new material or is a representation of an old subject of timely interest.
2. Whether the manuscript requires rewriting or careful editing.
3. Whether the subject matter can be condensed to advantage.
4. Whether there are any inaccuracies of statement which may be called to the author's attention.
5. Whether there is any phase of the subject which should be included.
6. Whether he recommends the paper for publication.

After the reviewer has completed his job he returns the manuscript to the divisional representative who then bases his appraisal of the paper on these reviews. Occasionally, particularly when the reviewers are not in agreement, he must make his own independent appraisal to reach a decision. If the paper needs only minor corrections, the representative takes these up directly with the author. Grammatical errors, spelling and punctuation generally are corrected without referring to the author. If the objections to the manuscript are more serious in nature, the representative has the option of either taking these up with the author in an attempt to put the paper into acceptable shape, or of rejecting the paper. With experience it should be possible to formulate more definite rules for the guidance of the representative. After the representative and the author have put the paper into acceptable form or if the paper is rejected, the representative sends the manuscript to the Chairman of the Publication Committee together with his recommendation and copies of the several reviews. The Chairman may reject the action of representative and return it to him for further consideration. Otherwise he returns the paper to the Secretary together with the recommendation of the Publication Committee as required in Section 16.

Upon receipt of the action of the Publication Committee the Secretary, in accordance with the provisions of Section 16, advises the author of the action taken. If the manuscript is accepted it is given a final editing in the Secretary's office by one of the editorial staff. Otherwise the rejected paper is returned to the author for revision or rewriting, or it may be rejected completely. The author is furnished

O. W. Storey, Chairman
Publication Committee

with copies of the reviewers' reports (the reviewers' names being withheld, however). A revised or rewritten paper must be submitted again to the Publication Committee.

Acceptibility Doubted

Where there is a wide divergence of opinion as to the acceptability of a paper, particularly where a matter of policy is concerned, the entire Publication Committee may be asked to express its opinion. This happens infrequently but the action in these cases sets the policies of the Society, and it particularly interprets the provisions of the By-Laws relating to the acceptability of papers as quoted above.

Naturally there is a wide divergence

of opinion within the Society as to what constitutes an acceptable paper. It, therefore, appears to me to be the function of the Publication Committee to maintain a standard which they believe meets the approval of the greatest number of members as expressed by them from time to time.

MODERN ELECTROPLATING

The monograph, *Modern Electroplating*, is a bound volume of the papers of twenty-six authorities in the field of electroplating presented before a symposium on electroplating held during the Eightieth Meeting of the Electrochemical Society at Chicago, Illinois, October 1–4, 1941. It includes also the entire discussion of these papers. While these papers were included in volume 80 of the Transactions of the Society, it was realized that they would be of great interest to a far larger audience. Consequently, the Board of Directors authorized an extra printing of the papers and discussion bound as a monograph entitled "*Modern Electroplating*". Before this volume appeared in June 1942, more than 900 subscriptions were taken. Since then its popularity has continued and a total of 4875 copies have been sold. The remaining supply will be exhausted early in 1948 after which it will be out of print and unavailable. While it is difficult to estimate accurately the profit to the Society of this publication venture, it is believed to amount to approximately $15,000.

EDISON MEDAL AWARDED DR. JOSEPH SLEPIAN OF WESTINGHOUSE

The Edison Medal for 1947, one of the nation's top engineering honors for meritorious achievement in electrical science, has been awarded to Dr. Joseph Slepian, associate director of the Westinghouse Research Laboratories, it was announced today by the American Institute of Electrical Engineers, sponsors of the award.

Dr. Slepian a member of the Electrochemical Society, was selected as the 37th winner of the Medal "for his practical and theoretical contributions to power systems through circuit analysis, arc control, and current interruption." He developed the Ignitron, an electronic tube now widely used in the production of aluminum and magnesium, and did outstanding pioneer work in the design of circuit breakers and lightning arresters for the protection of power systems. Dr. Slepian received the Medal on January 28, 1948, during the winter convention of the American Institute of Electrical Engineers in Pittsburgh, Pa. Founded in 1909 by associates and friends of Thomas A. Edison, the Medal is awarded annually for "meritorious achievement in electrical science, electrical engineering, or the electrical arts." Past winners include Alexander Graham Bell, Nikola Tesla, and George Westinghouse. Although Dr. Slepian has won several top engineering awards, including the John Scott Medal and the Lamme Medal, he

Dr. Joseph Slepian
Associate Director
Westinghouse Research Laboratories

was never formally trained as an electrical engineer.

Born in Boston, Mass., February 11, 1891, son of an immigrant Russian tailor, he was a brilliant student of mathematics and sciences in public schools. He graduated in 1911 from Harvard University and remained for graduate study, receiving the Ph.D. degree in mathematics in 1913. He studied abroad as a Sheldon fellow, the University of Gottingen in Germany and at the Sorbonne in Paris. Upon his return, Dr. Slepian became a mathematics instructor at Cornell University, but a few months later, in 1915, he resigned to be an apprentice at the East Pittsburgh Works of Westinghouse. How-

ever, his quick grasp of electrical engineering problems soon brought him to the attention of research and engineering officials and before long he was spending all his time in this work. In 1922 Dr. Slepian was appointed head of the general research section. Four years later he was made research consulting engineer and in 1938 became associate director of the laboratories.

Dr. Slepian is internationally known for his development of high-speed methods of extinguishing arcs in electric power systems. He conceived the first autovalve arrester—a stack of carborundum and clay discs that conducted high-voltage lightning currents to the ground, but stopped the passage of the lower voltage electricity flowing through the power line. His contributions helped make possible transmission of electric power at higher and more efficient voltages.

In 1932 he was awarded the John Scott Medal and the following year he won the AIEE national prize for the best paper in theory and research. He was elected to the National Academy of Science in 1941. The Benjamin Garver Lamme Medal, awarded annually by the AIEE for outstanding achievement in the development of electrical apparatus and machinery was presented to Dr. Slepian in 1943. During the war Dr. Slepian carried on important work for the atomic bomb project, spending a year at Berkeley, Calif., with Dr. Ernest O. Lawrence on the separation of atomic materials. He also served as a consultant to the Office of Scientific Research and Development and as a dollar-a-year man with the War Production Board.

DR. WESLEY G. FRANCE

Wesley G. France, professor of colloid and electrochemistry and member of the Ohio State University faculty since 1920, died at his home in Columbus, Ohio, December 4, 1947. Dr. France was a member of the American Chemical Society, as well as of the Electrochemical Society, and a past president of Sigma Xi. He was the author of numerous technical papers and coauthor of two books. He came to Ohio State from the University of Michigan where he had been on the faculty for three years.

DR. S. LAWRENCE BIGELOW

It is with regret that we announce the death on December 3, 1947, of Dr. S. Lawrence Bigelow of West Hartford, Connecticut. Dr. Bigelow became a member of this Society in May, 1903.

LOUIS G. SCOTT

It is with regret that we announce the death of Louis G. Scott during the year 1947. Mr. Scott became a member of this Society in February, 1922, and was engineer and Business Manager of E. G. Acheson Ltd., Westminster, London.

PERSONALS

R. B. HOXENG, formerly with the Aluminum Research Laboratories, New Kensington, Pa., is now a member of the staff of the Department of Chemistry and Chemical Engineering, Case Institute of Technology, Cleveland, Ohio.

ANANT T. PATHAK, who came to the United States in 1945 to work in electrochemistry at Columbia University under Dr. C. G. Fink, has recently completed his work at the National Bureau of Standards with Dr. William Blum and Dr. George Vinal. He is now returning to Bombay, India, to devote his efforts to research, development, and manufacture for the Indian government.

JAMES T. WABER, Assistant Research Professor, Illinois Institute of Technology, Chicago, Ill., until December 31, 1947, and KARL S. BERGSTRESSER, formerly research chemist of the Foote Mineral Company, Philadelphia, Pa., have announced that they have joined the research group at Los Alamos Scientific Laboratory, Los Alamos, New Mexico.

FRANK F. COLCORD, Vice President and Manager of metal sales of the United States Smelting Refining and Mining Company, New York, has established his residence at Covina, California.

KENNETH M. HUSTON is now connected with the American Rolling Mill Company, Rustless Iron & Steel Division, Baltimore, Md.

GEORGE J. EASTER, formerly Manager of Research and Development, The Carborundum Company, Niagara Falls, New York, is now Director of Research, Electro Refractories & Alloys Corporation, Buffalo, New York.

FARADAY SOCIETY DISCUSSES

Colloidal Crystallites and Micelles

The Faraday Society held a general discussion on "Colloidal Crystallites and Micelles" at the University of London, December 19, 1947. The program consisted of two chief divisions. Included in the first, "The Micelle in Solution" were eight papers of a theoretical nature with obvious practical applications, such as the reaction of dyes with wool and adsorption reactions of proteins with paraffin-chain salts.

The second division of the program consisted of nine papers under the main subject "Crystallinity in Solid Colloids." Solution and diffusion in high polymers, sorption of large molecules by keratin, and microscopic studies of the solution of nitrocotton by nitroglycerine were among papers included in this group. It was stated that the papers in this symposium were intended to fulfil in part the demand for an increase in the number of General Discussions held by the Faraday Society and were included in the list already approved for publication.

LATE ADDITIONS TO PROGRAM OF BATTERY SYMPOSIUM

Chicago, Feb. 7, 1948

"*The Determination of the Efficiency of Storage Battery Vent Plugs*"—Dr. Upton B. Thomas, Bell Telephone Laboratories, Murray Hill, New Jersey.

This paper presents a method for determining the efficiency of storage battery vent plugs.

"*The Development of the RM Cell During the War*"—Grenville B. Ellis, Chief, Battery Branch, Squier Signal Laboratory, Fort Monmouth, New Jersey.

This is an historical paper and presents the reasons why the RM cell was developed and indicates the rôle that the Signal Corps had in its development.

A.A.A.S. CENTENNIAL ANNIVERSARY

Washington, D. C., September 13–17, 1948

The unifying influence of science that is independent of national boundaries is the general theme of the Centennial Meeting in Washington, D. C., September 13–17, 1948, of the American Association for the Advancement of Science. Leading authorities in various branches of science will also present timely surveys of problems in their own fields of specialization. Afternoons will be free of scheduled sessions to permit attending scientists to visit the research institutions of the Capitol area on large scale openhouse invitations. Emphasis will be placed on the great responsibilities of scientists to society—*Science for Peace!*

Officers of the A.A.A.S. hope that all affiliated and associated societies will cosponsor the celebration of the Centennial Anniversary of the founding of the American Association as a milestone in American Science and aid in making this the greatest meeting of scientists ever held in this country.

INTERNATIONAL CONFERENCE ON SURFACE REACTIONS

Pittsburgh, Pa., June 7–11, 1948

The Pittsburgh International Conference on Surface Reactions will be held at the Mellon Institute for Industrial Research in Pittsburgh, June 7–11, 1948.

The Conference Committee is made up of the following: Dr. Earl Gulbransen (Westinghouse Research Laboratories) *Chairman*, representing *The Electrochemical Society, Pittsburgh Section;* Prof. D. S. McKinney (Carnegie Institute of Technology) representing The University Conference on Corrosion and Metal Protection; Prof. Mars G. Fontana (Ohio State University) representing *The Electrochemical Society, Corrosion Division;* J. M. Bialosky (Research Laboratory, Carnegie-Illinois Steel Company) representing The National Association of Corrosion Engineers; Dr. J. W. Hickman (Westinghouse Research Laboratories) representing The Pittsburgh Physical Society; C. Pogocar (Mellon Institute for Industrial Research) representing The American Society for Metals, Pittsburgh Chapter; Dr. George H. Young (Mellon Institute for Industrial Research) representing The American Chemical Society, Pittsburgh Section; Richard Rimbach (Corrosion Publishing Company) representing The Corrosion Forum.

Preliminary plans call for technical sessions mornings and evenings and visits to Pittsburgh research laboratories, which are working on surface reactions, in the afternoons. Scientists, engineers and educators from many parts of the world have been invited to participate in the Conference and

several will present papers.—Richard Rimbach, *Secretary*, Pittsburgh International Conference on Surface Reactions, 1117 Wolfendale Street, Pittsburgh 12, Pa.

FUTURE MEETINGS OF THE ELECTROCHEMICAL SOCIETY

Columbus, Apr. 14–17, 1948, Deshler-Wallick, C. L. Faust, *Chairman*.
New York, Oct. 13–16, 1948, Pennsylvania, K. G. Compton, *Chairman*.
Philadelphia, Apr. 13–16, 1949, Pending, Ernest G. Enck, *Chairman*.
Chicago, Oct. 12–15, 1949, LaSalle, Clifford Hampel, *Chairman*.
Buffalo, N. Y., Oct. 11–14, 1950, Statler.
Sessions on Corrosion, Electronics and Electrothermics will be held at the Spring Conventions. Sessions on Electro-Organics, Electrolytic Cells and Electrodeposition at the Fall Conventions.

MEETINGS OF OTHER SCIENTIFIC SOCIETIES

March 18–20, Ohio Society of Professional Engrs., Netherland Plaza Hotel, Cincinnati, Ohio.
March 22–25, Institute of Radio Engineers, 1 E. 79th St., New York, N. Y.
March 26–27, Pennsylvania Academy of Science, Grove City College, Grove City, Pa.
April 19–23, American College of Physicians, San Francisco, Calif.
April 21–23, National Petroleum Association, Hotel Cleveland, Cleveland, Ohio.
April 24, Society for the Advancement of Education, Inc., 15 Amsterdam Ave., New York, N. Y.
April 25–30, American Ceramic Society, Palmer House, Chicago, Ill.
April 26–28, National Academy of Sciences, 2101 Constitution Ave., Wash., D. C.
April 26–29, American Association of Petroleum Geologists, Shirley-Sevoy Hotel, Denver, Colorado.
April, American Coordinating Committee on Corrosion, St. Louis, Mo.
April 30–May 1, West Virginia Academy of Science, West Va. School of Technology, Montgomery, W. Va.
May, New York State Society of Professional Engineers, 1941 Grand Central Terminal Bldg., New York, N. Y.
May, American Radio Relay League, Inc., 38 LaSalle Road, West Hartford, Conn.
May 26–27, American Iron & Steel Institute, Waldorf Astoria, New York, N. Y.
June 14–18, American Society for Engineering Education, Univ. of Texas, Austin, Texas.
June 18–20, American College of Radiology, Continental Hotel, Chicago, Ill.
June 21–25, American Society for Testing Materials, Detroit, Mich.
June, Alpha Chi Sigma Fraternity, Tudor Arms Hotel, Cleveland, Ohio.

A.I.E.E. MEETINGS—1948

Meetings of the American Institute of Electrical Engineers to be held in 1948 are:
Winter General Meeting, Pittsburgh, Pa., Jan. 26–30.
Great Lakes District Meeting, Des Moines, Ia., April 1–3.
North Eastern District Meeting, New Haven, Conn., April 28–30.
Summer General Meeting, Mexico City, Mex., June 21–25.
Pacific General Meeting, Spokane, Wash., Aug. 24–27.
Middle Eastern District Meeting, Washington, D. C., Oct. 5–7.
Midwest General Meeting, Milwaukee, Wis., Oct. 18–22.
Southern District Meeting, Birmingham, Ala., Nov. 3–5.

OUTSTANDING EXHIBITS AT CHEMICAL INDUSTRIES EXPOSITION

The twenty-first Chemical Exposition held at Grand Central Palace, New York, during the first week of December, attracted capacity attendance. As usual there were many new developments of special interest to electrochemists. Only a few can be mentioned. The National Carbon Company exhibited new designs of heat exchangers suitable for plating bath installations. "Karbate" sectional cascade cooler was a spectacular demonstration. Also among the many products of service to the chemical industry were spectroscopic electrodes and powders and ground rods for cathodic protection applicable to electrochemical operations.

Aluminum anodes for cathodic protection of steel water tanks and buried pipe conveyors were displayed. Experimental use of these anodes in over 1000 installations subjected to over 1100 ampere hours per pound has demonstrated their serviceability, and this relatively recent development should be

of great value to the chemical, electrical, and electrochemical industries. An interesting patented use of hydrated alumina powder as a polishing agent and neutralizing constituent of a nationally known dentifrice was displayed.

One of the exhibits in motion which attracted groups of interested spectators continuously was the mechanical "braiding" by action of revolving spools of white and colored Fiberglas "yarns for the production of glass electrical insulation "sleeving." Owens-Corning Fiberglas fibers are first twisted to form "yarn," as it is termed, which is then surface dyed with organic dyes. Inorganic dyes, for example silicones, have a potential use in glass dyeing and are now in an experimental stage of development. Much softer "fibers" are produced with inorganic dyes.

Another "active exhibit which demonstrated good showmanship and had a strong interest appeal was the solidification of a viscose rayon solution as it passed through a platinum spinneret into a sulfuric acid bath and was wound on a spool as tiny rayon fibers. This was displayed by the International Nickel Company which also exhibited corrosion resisting equipment. Other exhibitors of corrosion resisting equipment were Duriron Company, Inc., producers of Durimet and Durco alloys; Haynes Stellite Co., whose Hastelloy high-strength alloys are well known; Lapp Process Equipment, makers of chemical porcelain, noncorrosive equipment.

Demonstrating the current trend toward instrumental methods of analysis were several exhibits of elaborate and recent special types of apparatus. The RCA Electron Microscope which displayed illuminated color transparencies of the Universal and Console models continued to attract and interest groups of spectators. Neutral transparencies of electron micrographs of carbon particles, magnified 60,000 times, kaolin (20,000 ×), zinc oxide smoke (30,000 ×), magnesium oxide smoke (49,000 ×), high purity nickel, and aluminum oxide monohydrate illustrated the clarity of images and extent of magnification obtainable with this most valuable and remarkable tool for chemical and bacteriological identification and analysis. Technicon Company, New York, exhibited an automatic chromatographic analyzer with a capacity of 200 tubes for collection of eluate, each tube being 20 ml size. Only one of these instruments is at present in use at the Rockefeller Institute for Medical Research, New York, but 25 others are ready for immediate delivery.

The General Electric Company's apparatus exhibit included an x-ray photometer for the rapid determination of one element or compound in the presence of others using specimens in gaseous, liquid, or solid state. Results are said to be obtainable in a few seconds. Typical uses are the determination of the ash content of coal, heavy metals in glass, silver in solutions, and chlorine in plastics. As all chemical industries have need for such analyses, this valuable and elaborate piece of apparatus is of great interest to those who can possess it. The General Electric Company also displayed an ACA motor, adjustable speed motor, considered by them as their most interesting exhibit. The motor, as indicated, allows speed adjustment to meet changing needs during the course of an operation or operations. An electromagnetic torque meter for measurement of the amount of torque applied in any given process was also on display at this booth.

In a corner of the rear of the first floor, the American Chemical Society's exhibit effectively publicized the work of the Society in aiding chemists to make outstanding scientific accomplishments and contributions to chemical literature. Many visitors were attracted by the significant legend arched above a display of the Society s enviable array of publications. "The Chemical Industry of Today and Tomorrow is built on Yesteryear's Fundamental Research. Witness this Truth in the Story of Fluorine Chemistry and the Silicones as it unfolded from Fundamental Research to Commercial Production, on the Pages of the Publications of the ACS—the World's Greatest Storehouse of Modern Chemical Knowledge." Historical briefs on each side of this legend further proclaimed the story of the Silicones and Fluorine Chemistry. Also exhibited with just pride were the editorial award plaques to Chemical and Engineering News for the best series of articles published during the twelve months ending July 31, 1946, on Atomic Energy, and to Industrial and Engineering Chemistry for the best single issue published during the twelve months ending July 31, 1947, on Industrial Wastes.

POSITIONS AVAILABLE

PHYSICAL AND ELECTROCHEMISTS FOR RESEARCH. Training or experience in electrolysis of metals in fused salts will be of value. Excellent opportunity in laboratory located in New Jersey. Submit qualifications and salary expected. Reply to Box A-198, Electrochemical Society, Inc., 235 West 102nd St., New York 25, N. Y.

POSITIONS WANTED

Electrochemist: B.Sc., PhD. (London) desires position in America as consultant and/or technical adviser for research and development divisions of electrochemical and chemical process industries. Author of technical publications, including brass plating processes, bonding of rubber to metals. Fluent knowledge of French, German and Roumanian. Nine years industrial experience. Age 35; married; residing in London. Reply to Box 316, Electrochemical Society, Inc., 235 West 102nd St., New York 25, N. Y.

PATENTS OF INTEREST TO ELECTROCHEMISTS

Selected by Fred W. Dodson, Chairman of the Patent Committee, from the Official Gazette

December 2, 1947

Pugh, M. L., 2,431,707, Battery Charging Apparatus

Yerkes, L. A., 2,431,723, Electrolytic Method for Producing Magnesium Alloys

Little, J. H., and Rady, W. J., 2,431,945, Thermal Control Device for Storage Batteries

Martz, W. M., 2,431,947, Formation of a Strong Bond between a Ferrous Metal Surface and an Electrodeposit of Silver

Martz, W. M., 2,431,948, Apparatus for Electrodepositing Metal on Bearing Shells and the Like

Martz, W. M., 2,431,949, Apparatus for Electroplating the Inside of Bearing Shells and the Like

McAninch, O. G., 2,431,953, High-frequency Thermocouple

Hanson, V. F., 2,432,013, Measurement of Leakage Resistance in Electrolytic Cell Systems

Pugh, M. L., 2,432,068, Battery Testing and Charging System

Pugh, M. L., 2,432,069, Battery Charger

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Tama, Manuel and Tama, Mario, Re. 22,948, Submerged Resistor Type Induction Furnace and Method of Operating

Loevenstein, Hirsch, 2,432,111, Furnace for Reducing and Distilling Volatile Metals

Evans, F. C., 2,432,145, Fire Detector of the Thermocouple Type

Griffiths, W. T., and Pfeil, L. B., 2,432,149, Heat Resistant Nickel Alloys

Lundstrom, J. V., 2,432,322, Apparatus for Electroplating Articles having Pockets or Recesses therein

MacMullin, R. B., 2,432,431, Cell for the Electrolysis of Magnesium Chloride Fusions

December 16, 1947

Franks, Russell, and Binder, W. O., 2,432,614, Ferrous Alloys for High-Temperature Service

Franks, Russell, and Binder, W. O., 2,432,615, Iron-Base Alloys

Franks, Russell, and Binder, W. O., 2,432,616, Ferrous Alloys for Use at High Temperatures

Franks, Russell, and Binder, W. O., 2,432,617, Ferrous Alloys for High-Temperature Use

Franks, Russell, and Binder, W. O., 2,432,618, Ferrous Alloys for High-Temperature Use

Franks, Russell, and Binder, W. O., 2,432,619, Ferrous Alloys and Articles

Blackburn, Newell F., 2,432,718, Tin-Plating Process

Holt, M. L. and Nielsen, M. L., 2,432,893, Electrodeposition of Nickel-Tungsten Alloys

Holt, M. L. and Black, R. E., 2,432,894, Electrodeposition of Iron-Tungsten Alloys

Smedberg, G. E., 2,432,973, Apparatus for Feeding Granular Salt into a Fused Salt Electrolysis Cell

NEW BOOKS

Bennett, H., *Concise Chemical and Technical Dictionary*, Brooklyn, N. Y., Chemical Publishing Co. $10.00.

Kirk, R. E., and Othmer, D. F., *Encyclopedia of Chemical Technology*, 10 volumes, New York, The Interscience Encyclopedia, Inc., volume 1, fall, 1947. $20.00 per volume.

Groggins, P. H., *Unit Processes in Organic Synthesis*, New York, McGraw-Hill, 1947. 3d ed (Chemical engineering series.) $6.50.

Eastman, E. D., and Rollefson, G. K., *Physical Chemistry*, New York. Mc-

Graw-Hill, 1947. (International chemical series.) $4.50. (Written as a college text.)

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NEW MEMBERS

At the meeting of the Executive Committee held on January 9, 1948, at the office of The Electrochemical Society, Inc., 235 West 102nd St., New York City, the following were elected to membership:

RICHARD R. CLUNE, P. R. Mallory & Co., Inc.; mailing add.: Hunters Lane, Elmsford, N. Y. (Batteries)

ALVIN, GLASSNER, Trinity College, Dept. of Chem., Hartford 6, Conn. (Theoret. Electrochem., Batteries, Corrosion)

WALTER B. LLEINER, American Smelting & Refining Co., mailing add.: 1845 First St., Plainfield, N. J. (Organic Electrochem., Batteries, Theoret. Electrochem., Electrodep., Electronics)

EVERETT KEITH MCMAHON, Columbia University, Box 102 Havemeyer Hall, N. Y. C. (Theoret. Electrochem., Organic Electrochem., Electronics, Dielectrics)

LOUIS ROBERT MANNHEIM, Nickel Cadmium Battery Division, mailing add.: 77 E. Pleasant St., Amherst, Mass. (Batteries, Corrosion, Alkali and Chlorine, Dielectrics)

JAMES RAYMOND NEWBERRY, Mathieson Alkali Works, 1008 United Office Bldg., Niagara Falls, N. Y. (Alkali and Chlorine, Electrodep.)

WALTER A. RAYMOND, Finishing Publications, 11 W. 42nd St., N. Y. C. (Theoretical Electrochem., Corrosion, Electrodep.)

SAMUEL RUBEN, Ruben Laboratories; mailing add.: 265 Storer Ave., New Rochelle, N. Y. (Theoret. Electrochem., Batteries, Electronics)

ALBERT BARRON SAMPLE, Smith, Kline & French Labs., 800 No. Delaware Ave., Phila. 23, Pa. (Theoret. Electrochem., Organic Electrochem., Electronics)

SUDHIR CHANDRA SHOME, 910 Fernald Hall, Columbia University, N. Y. C. (Electrodeposition and Electrothermics)

SHIH JIEN WANG, Columbia University; mailing add.: 370 Riverside Dr., N. Y. C. (Theoret. Electrochem., Alkali and Chlorine, Electrodep.)

LEONARD G. WISE, E. I. du Pont de Nemours & Co., Chem. Dept. Experimental Sta., Wilmington, Dela. (Theoretical Electrochem., Organic Electrochem.)

REPORT ON RESPONSE TO MEMBERSHIP QUESTIONNAIRE OF APRIL 1947

Submitted by the Ways and Means Committee

It will be recalled that a questionnaire was sent to the members of the Society in April, 1947, for the purpose of learning their views and desires upon the organi-

zation, activities, management and publication policies of the Society. Returns were received from 972 members out of 2233 to whom questionnaires were mailed. This is a good showing and reflects a widespread interest among the members in the affairs of the Society. Only in the last election of national officers did more than 400 members vote, and then the total was less than 500. For the most part, the replies showed helpful suggestions and constructive criticism. From the replies to several questions, it is apparent that major changes in policy are needed.

The members desire the management of the Society to be in the hands of the Board of Directors. They also went a better and coördinated national policy for planning with local sections.

Dissatisfaction was widespread concerning publication policy. Particular reference was made to delays in handling and in printing. These were thought to be unduly long in spite of the restrictions imposed by national conditions. Better selection and editing by the Divisions was demanded.

Establishment of the new publication in which this appears should go a long way toward meeting this criticism. It will also allow wider guidance on subject matter and editing. Review and acceptance of manuscripts by division representatives, as provided in the reorganized Publication Committee, described elsewhere in this issue, makes the Divisions directly responsible for technical quality of the articles in the monthly publication and in the Transactions.

The distribution of the membership according to divisional interest, age group, and activity, shown in Table 1, reveals that the response to the questionnaire is representative of the membership of the Society. The need was shown for a new division, Batteries, and this has since been organized.

TABLE 1. *Divisional Interest and age distribution of members who responded to questionnaire*

Division	Total	Number of Replies by Age Group		
		20–30	30–40	Over 40
Corrosion	189	18	83	88
Electrodeposition	331	34	153	144
Industrial electrolysis	146	7	45	94
Electrothermics	91	2	21	68
Electronics	46	4	15	27
Electro-organic	24	3	4	17
Theoretical electrochemistry	69	7	28	34
Batteries*	13	1	7	5
Miscellaneous†	63			
Total‡	972	76	356	477

* Batteries was not a listed Division on the Questionnaire. The eleven members wrote it in as their "division."

† This refers to those questionnaires on which none or more than one divisional interest was checked.

‡ Includes 22 replies from members outside of North America.

TABLE 2. *Question 2. How do you characterize the nature of your employment? (Check more than one, if appropriate)*

Division	Teaching	Industrial, manufacturing	Industrial research	Consulting	Sales	Administrative
Electrodeposition	20	125	126	57	33	56
Corrosion	15	40	109	27	5	23
Electrothermics	3	22	40	14	6	19
Industrial electrolysis	4	58	68	7	9	38
Theoretical electrochemistry	27	6	28	12	0	13
Electronics	0	12	23	6	1	12
Electro-organic	7	3	7	6	1	5
Batteries	1	5	10	1	0	0
Miscellaneous	5	11	25	17	3	20
Totals	82	283	436	147	58	186

Table 2 (Question 2 on the nature of employment) shows a well-balanced coverage for a technical society. Industrial research commands the largest number, but the diversity of value of Society membership is a matter of practical significance. There is ample incentive shown here for the officers and members to continue their efforts

for maintaining the eminence of the Society.

The majority of active members apparently are over 30 and about equally divided between the groups, "30 to 40" and "over 40". Thus, there is an indicated need for a program to interest the younger men in the electrochemical field.

Question 4. Are you answering this as an individual or as a representative of a library, or business, or research corporation, or educational institution?

Replies to this question were overwhelmingly checked as "*an individual.*" Therefore, tabulations were not made for detail division of answers. For all practical purposes, individual opinion is presented, illustrating that, although many industrial firms offer support as sustaining members, company policies are not inflicted as political influences in the Society.

Question 5 was found to be difficult for any member to answer with broad implication. But the outstanding opinion was that the Society offers real benefits to its members (see Table 3).

Replies to *Question 6* (see Table 4) essentially show that the members over 30 consider that the Society on its present plane can serve the young members. This conclusion may be questioned because there are relatively few replies from younger members.

Question 7. "If your answer to (6) is "No," what suggestions do you offer to remedy this situation?" Replies show interesting and helpful suggestions of which the following were most pertinent: "Younger blood needed in official capacity." "Need better local sections for young members who generally can seldom attend national meetings." "Suggest planned program to interest young chemists in related fields." "The younger members should be on committees." "National Society is too remote from sections. Need further spreading of responsibilities into younger age groups." "Local sections should combine programs." "National meetings should have technical sessions concurrently, so that something of interest would be going on for each member."

"Local sections have no direct representation in the National Society." "An educational conference at conventions would be helpful." "More interesting local group meetings." "Sponsor scholarships and promote student interests." "Arrange a series of texts and help improve teaching methods by means of technical films." "More symposia and more publications on fundamentals." (Suggests junior memberships at reduced dues up to 25 years of age.) "Officers should endeavor to meet and talk more with younger members." "Better coördination between headquarters and sections." "Elect Board of Directors by age group representative of age composition of the Society." "Better get-acquainted efforts at national meetings. "More local groups." "Special attention at conventions for assisting younger men to meet older members.

"More technical information for background material." "Articles by leading members on future of electrochemistry

TABLE 3. *Question 5. Does the Society now serve the needs and wishes of the Members?*

Division	Total			Age group					
				20–30		30–40		40+	
	Yes	No	No opinion	Yes	No	Yes	No	Yes	No
Corrosion	118	25	17	11	3	51	12	56	10
Electrodeposition	220	34	24	18	3	101	20	101	11
Industrial electrolysis	89	22	15	4	0	24	14	61	8
Electrothermics	59	7	12	2	0	13	2	44	5
Electronics	33	4	3	3	1	11	1	19	2
Electro-organic	17	3	2	3	0	3	1	11	2
Theoretical electrochemistry	45	14	4	4	1	22	3	19	10
Batteries	9	1	1	1	0	5	1	3	0
Miscellaneous	35	4	21						
Totals	625	114	99	46	8	230	54	314	48

as a professional field." "More correlation and reports on activities of different branches. More papers and articles on general electrochemistry." "Aims of divisions should be published so members can know." "More aggressive ety too specialized for student branches, yet student affiliation should be fostered."

An interesting implication in replies to *Question 7* is that more opportunity should be given to the Divisions to

TABLE 4. *Question 6. Are the younger members served as well as possible in a Society having several Divisions, wide geographic distribution, and a broad age group?*

Division	Total			Age group					
	Yes	No	No opinion	20–30		30–40		40+	
				Yes	No	Yes	No	Yes	No
Corrosion	98	36	29	10	5	41	19	47	12
Electrodeposition	193	37	48	16	4	90	24	87	9
Industrial electrolysis	80	27	19	5	0	24	15	51	12
Electrothermics	48	10	20	2	0	11	3	35	7
Electronics	24	5	11	3	1	9	1	12	3
Electro-organic	17	3	2	3	0	1	1	12	2
Theoretical electrochemistry	36	15	11	1	2	20	5	15	9
Batteries	6	2	3	1	0	2	2	3	0
Miscellaneous	24	9	27						
Total	526	144	170	41	12	199	70	262	54

TABLE 5. *Question 8. In your opinion, do the Divisions take a sufficiently active position in the technical program of the Society?*

Division	Total			Age group					
	Yes	No	No opinion	20–30		30–40		40+	
				Yes	No	Yes	No	Yes	No
Corrosion	102	41	20	9	4	44	17	40	20
Electrodeposition	158	72	48	11	9	72	37	75	26
Industrial electrolysis	70	34	22	3	2	22	12	45	20
Electrothermics	40	25	15	2	0	7	6	31	19
Electronics	28	8	4	1	3	11	1	16	4
Electro-organic	16	4	2	2	0	3	1	11	3
Theoretical electrochemistry	34	16	11	2	2	18	5	14	9
Batteries	7	4	0	1	0	3	3	3	1
Miscellaneous	23	9	28	1	0	5	1	17	8
Total	478	213	150	32	20	185	83	261	110

national policy and a good monthly publication. Discussion of policy in the publications." "Better coördination and directions at headquarters." "Encourage more education in electrochemistry." "More and better regional meetings." "Young members never will be satisfied, but this is a healthy situation." "One national meeting a year and more regional meetings." "More emphasis on section meetings." "Soci- arrange the technical program, each for its own field.

The replies to *Question 8* (see Table 5) show a majority opinion that the Divisions are active in the Society's technical program. Yet the large number of "no's" clearly imply that more responsibility should be assigned to the Divisions.

The technical standing of the Society is good, according to most members as

shown by *Question 9* (Table 6). Many considered that the Society has been stationary during the past few years, and that new energy is needed for maintaining the present good position.

Question 10 (Table 7) reveals that the members consider for the most part that national officers do their job well, but the members do not have a good picture of what the national officers are supposed to do or of what transpires at Board Meetings. "Maybe we should not expect much more from voluntary services rendered by busy men. But the fact remains the Society is not forging ahead."

According to *Question 10*, the national officers received a vote of confidence, but there was plenty of comment that room exists for improvement. The direction is shown by replies to *Question 11*.

Question 11. Returns show that the management should be in the hands of the Board of Directors, with the Secretary's office carrying out the duties prescribed and with routine assistance provided by a paid Assistant Secretary as provided in the Constitution.

In general, replies to *Question 12* (Table 8) show that a good balance exists for divisional activities. The most active divisions contribute the most.

Question 13. If your answer to (12) is "Yes," your comments on *what group*

TABLE 6. *Question 9. Do you consider that the Society has maintained its standing the last few years?*

Division	Total			Age group					
	Yes	No	No opinion	20–30		30–40		40+	
				Yes	No	Yes	No	Yes	No
Corrosion	126	30	7	11	4	56	11	59	15
Electrodeposition	210	46	22	17	4	103	19	90	23
Industrial electrolysis	100	42	6	6	0	29	7	65	13
Electrothermics	57	15	6	2	0	13	3	42	12
Electronics	35	5	0	4	1	12	1	19	3
Electro-organic	20	1	1	3	0	3	0	14	1
Theoretical electrochemistry	44	13	6	4	1	21	4	19	8
Batteries	20	1	0	1	0	4	1	5	0
Miscellaneous	34	10	16	0	1	5	2	29	7
Total	646	163	64	48	11	246	48	342	82

TABLE 7. *Question 10. Do you think that the national officers are doing: A good job; fair job; poor job?*

Division	Totals				Age Group								
	N.P.	G.	F.	P.	20–30			30–40			40+		
					G.	F.	P.	G.	F.	P.	G.	F.	P.
Corrosion	11	87	58	7	10	4	0	37	27	3	40	27	4
Electrodeposition	15	169	86	8	14	7	0	74	44	4	81	35	4
Industrial electrolysis	4	73	45	4	5	1	0	16	17	3	52	27	1
Electrothermics	6	41	30	1	2	0	0	7	10	0	32	20	1
Electronics	1	27	10	2	2	1	1	8	4	0	17	5	1
Electro-organic	0	12	10	0	2	1	0	3	1	0	7	8	0
Theoretical electrochemistry	5	32	20	6	1	3	1	17	7	2	14	10	3
Batteries	0	6	5	0	1	0	0	3	3	0	2	2	0
Miscellaneous	17	30	9	4									
Total	59	477	273	32	37	17	2	175	114	12	245	134	14

N.P. = no opinion. G. = good job. F. = fair job. P. = poor job.

will be very helpful in guiding future policy. Many replies show evidence of poor thinking on this question. Qualifying comments in numerous cases said "Yes, but only because the division is active." "Any division that feels to become active and aggressive. The members obviously want a balanced society and will support one.

Replies to *Question* 14 (Table 9) reveal that the publications of the Society are the most useful return to the mem-

TABLE 8. *Question 12. In your opinion is undue emphasis given to the interest of any one division?*

Division	Total			Age group					
	Yes	No	No opinion	20–30		30–40		40+	
				Yes	No	Yes	No	Yes	No
Corrosion	18	134	11	1	19	9	56	8	59
Electrodeposition	17	228	33	2	19	10	106	5	103
Industrial electrolysis	19	95	12	2	4	7	28	10	63
Electrothermics	12	52	14	0	2	2	10	10	40
Electronics	4	29	7	2	3	1	9	1	17
Electro-organic	2	18	2	0	3	0	3	2	12
Theoretical electrochemistry	8	49	6	0	3	3	22	5	24
Batteries	1	8	2	0	1	1	5	0	2
Miscellaneous	0	36	24						
Total	81	649	111	7	54	33	239	41	320

TABLE 9. *Question 14. In which ways does the Society benefit you? Check as many as apply. Publications; Contacts; Technical meetings; Educational*

Division	Total					Age group											
	N.P.	P.	C.	T.	E.	20–30				30–40				40+			
						P.	C.	T.	E.	P.	C.	T.	C.	P.	C.	T.	E.
Corrosion	2	144	65	68	51	12	7	7	5	61	24	30	22	71	34	31	24
Electrodeposition	10	254	75	100	96	24	2	5	6	120	31	50	49	110	42	45	42
Industrial electrolysis	2	105	58	65	26	7	4	5	3	29	23	20	12	69	31	40	11
Electrothermics	6	62	24	30	14	2	0	0	1	13	4	6	4	47	20	24	9
Electronics	5	36	21	19	12	4	2	2	3	12	3	4	0	20	16	13	9
Electro-organic	0	18	12	11	9	3	2	1	3	4	2	2	1	11	8	8	5
Theoretical electrochemistry	3	33	18	25	19	4	1	5	2	20	9	12	8	9	8	8	9
Batteries	1	10	6	6	5	1	1	1	1	6	3	3	2	3	2	2	2
Miscellaneous	7	45	14	17	11												
Totals	36	707	293	341	243	57	19	26	24	265	99	127	98	340	161	171	111

N.P. = no opinion. P. = publications. C. = contacts. T. = tech. meetings. E. = educational.

slighted should activate itself." "The most aggressive divisions get the most attention, and that is as it should be." "Enough emphasis is not given to any division." "Corrosion has not been given enough emphasis. If it had, the National Association of Corrosion Engineers might never have been started."

It is clear that the Society needs a policy that will encourage all divisions bers and that educational value of membership needs improvement.

According to *Question 15* (Table 10), the national conventions are not accessible to most members. Serious consideration should be given to one annual meeting and more regional meetings with national office guidance and interest. Members who attend conventions have offered good suggestions for im-

provement. These will be of interest to those arranging the technical sessions and to those making the general plans (Question 16).

and 18, the National Society has been very lax in fostering local sections and in contact with existing local sections. Liason has been poor. Improvement at

TABLE 10. *Question 15. Do you attend the national meetings? Twice a year. Once a year; Occasionally; Infrequently?*

Division	Total					Age Group											
						20-30				30-40				40+			
	No.	Tw.	One.	Occ.	Inf.	Tw.	One.	Occ.	Inf.	Tw.	One.	Occ.	Inf.	Tw.	One	Occ.	Inf.
Corrosion	10	3	28	73	49	0	3	5	7	0	13	38	13	3	12	30	29
Electrodeposition	28	9	42	109	90	0	3	8	11	6	19	56	31	3	20	45	48
Industrial electroylsis	5	11	29	55	26	0	2	4	0	4	11	15	7	7	16	36	19
Electrothermics	10	5	10	28	25	0	0	1	0	0	3	7	6	5	7	20	19
Electronics	5	2	5	20	8	0	1	1	1	0	2	5	2	2	2	14	4
Electro-organic	1	2	5	12	2	0	1	2	0	0	2	2	0	2	2	8	2
Theoretical electrochemistry	5	4	9	22	23	1	0	2	1	1	5	11	7	2	4	9	15
Batteries	1	1	2	6	1	0	1	0	0	0	1	4	1	1	0	2	0
Miscellaneous	13	4	1	25	17												
Total	78	41	131	350	241	1	11	23	21	11	56	138	67	25	63	164	136

No. = never. Tw. = twice yearly. One = once ayear. Occ. = occasionally. Inf. = infrequently.

NOTE: General indication is that members attending most regularly do so once a year when attention is focused on field of their interest.

TABLE 11. *Question 19. For the sake of continuity in understanding the affairs of the Society and its management policy, would you favor a procedure of officer succession through the Vice Presidencies to Presidency, not mandatory, but expected where abilities exist? Presidential caliber would be considered in nomination of Vice Presidents*

Division	Total			Age group					
				20-30		30-40		40+	
	Yes	No	No opinion	Yes	No	Yes	No	Yes	No
Corrosion	134	18	11	11	4	58	7	65	7
Electrodeposition	202	48	28	18	6	92	26	92	16
Industrial electrolysis	101	16	9	5	1	29	7	67	8
Electrothermics	58	11	9	2	0	13	2	42	9
Electronics	31	6	3	4	1	10	1	17	4
Electro-organic	19	2	1	3	0	2	1	14	1
Theoretical electrochemistry	49	8	6	5	0	22	3	24	5
Batteries	8	0	3	1	0	4	0	3	0
Miscellaneous	37	10	13	1	0	3	4	33	6
Total	639	119	83	50	12	233	51	357	56

Question 17. Do you attend local section meetings? Regularly; Irregularly?

Question 18. Have you any suggestions for improving local section meetings? If so, what?

According to replies for *Questions 17* local section level is offered as the best way for improving and strengthening the young member interest.

According to *Question 19* (Table 11) the members are overwhelmingly in favor of having the President be a member with some training in Society affairs

and interest by having once been a Board Member. A Vice President is a natural nominee for President.

10, clearly reveal that the membership considers the present publication policy to be inadequate, and that a prompt

TABLE 12. *Question 20. In view of higher costs in all categories these days, how would you react toward increasing dues? Favor nominal increase; Opposed to any increase*

Division	Total			Age group					
				20–30		30–40		40+	
	Yes	No	No opinion	Yes	No	Yes	No	Yes	No
Corrosion	73	85	5	8	7	28	40	37	38
Electrodeposition	123	142	13	6	18	49	74	68	50
Industrial electrolysis	74	48	4	3	3	19	18	52	27
Electrothermics	34	35	0	1	1	6	0	27	25
Electronics	20	20	0	2	3	6	6	12	11
Electro-organic	11	11	0	0	3	4	0	8	7
Theoretical electrochemistry	30	32	1	4	1	10	18	16	13
Batteries	3	7	1	0	1	2	4	1	2
Miscellaneous	24	24	12	0	1	1	4	23	19
Total	393	403	45	24	38	125	173	244	192

A large percentage of "yes" (favor nominal increase) replies were qualified by comment "only if absolutely necessary to maintain status quo". Some replies indicated resignation if dues were increased. Some replies suggest that the 20-30 age group and students should have a "lower dues" arrangement.

A number of replies stated that financial position of the society could not be ascertained from yearly statement and services recently have been inadequate for dues paid.

TABLE 13. *Question 21. Do you think special publications like Modern Electroplating are proper activities for the Society to sponsor?*

Division	Total			Age group					
				20–30		30–40		40+	
	Yes	No	No opinion	Yes	No	Yes	No	Yes	No
Corrosion	100	53	11	10	4	47	19	41	30
Electrodeposition	248	17	11	24	0	122	6	100	11
Industrial electrolysis	68	41	20	6	0	21	12	39	29
Electrothermics	42	22	15	1	0	12	3	27	19
Electronics	29	10	4	5	0	10	1	12	9
Electro-organic	15	9	0	3	0	3	1	7	8
Theoretical	42	16	6	4	1	17	7	19	8
Batteries	8	3	1	1	0	4	2	2	1
Miscellaneous	33	11	8	1	0	6	2	26	9
Total	583	182	76	55	5	242	53	273	124

A number of replies had never heard of *Modern Electroplating*, prepared by the Electrodeposition Division.

Since Corrosion Division is producing a handbook, the large number of "Nos" indicates that the activity is not well publicized among division members.

A large number of comments said "emphatically yes". Best book on electroplating. Need more like it from other Divisions. Many said "yes, if self-financing, showing that the cost and income of *Modern Electroplating* is not known to members."

Question 20 (Table 12) reveals opposition to increasing the dues.

Questions 21 and 22 (Tables 13 and 14), as well as comments in reply to *Question* monthly journal is highly desirable. Monograph publication and those like *Modern Electroplating* meet with wide approval as a Society or Division activ-

ity. The quality of the published articles has been acceptable during war years, but stricter reviewing is the general recommendation for the future to ensure only the best, even if fewer, papers. There is wide objection to presenting absentee-author papers at conventions and to vague timing of oral presentation permitting dull reading of manuscripts word by word. Most members want more time for discussion of papers at conventions.

The following are a few individual, specific replies to *Question 22* which illustrate the trend of comment. "Fair. Too many noncritical reviews. Technical quality cannot be improved until authors are aware of the editorial policy." "Fair. There are many cases where reviewers have turned down papers that later are published with little or no change. This is bad." "Fair. The standard of acceptance should be higher." "Good. The Society should manage an electrochemical show occasionally like the ASM Metals Show." "Good. Far above those of many national engineering societies." "Some good, some poor, indicating a lack of censorship." "Some very, very, poor editing: the volume should be cut down. This would improve quality." "Adopt a monthly journal to replace Bulletin and preprints." "Good. Better than most other technical societies." "Fair. Include more illustrations." "Fair. Some articles could well be eliminated." "Suggest membership lists be published more frequently." "Good. Would like to see more summary type articles and a few more of general interest." "Good. But too often out-of-date by the time they are available. The average article is two years old."

TABLE 14. *Question 22. Do you consider technical quality of articles now published to be: Good; Fair; Poor?*

Division	Totals				Age group								
					20–30			30–40			Over 40		
	N.O.	G	F	P	G	F	P	G	F	P	G	F	P
Corrosion	4	101	56	2	8	7	0	45	23	1	48	26	1
Electrodeposition	10	184	79	5	18	5	1	78	44	2	88	30	2
Industrial electrolysis	8	73	41	4	4	2	0	17	15	3	52	24	1
Electrothermics	15	36	25	2	2	0	0	6	8	1	28	17	1
Electronics	2	25	13	1	3	1	0	7	5	0	14	7	1
Electro-organic	0	14	3	5	2	1	0	3	1	0	9	1	5
Theoretical electrochemistry	2	30	20	11	3	1	1	13	8	5	14	11	5
Batteries	1	5	4	1	0	1	0	3	2	1	2	1	0
Miscellaneous	8	38	12	2									
Total	50	506	253	33	40	18	2	172	106	13	255	117	16

N.O. = No opinion. G = A good job. F = Fair job. P = Poor job.

ELECTROLYTIC ALLOY DEPOSITS OF TUNGSTEN WITH COBALT, NICKEL, AND IRON

An electrolytic bath is prepared by adding anhydrous tungstic acid gradually to a boiling sodium hydroxide solution. Concentrated sulfuric acid is then added dropwise and afterward tartaric and boric acids and cobalt sulfate. The pH is raised to 7.0 with sodium hydroxide and distilled water added to a volume of one liter. Platinum electrodes in conjunction with tungsten-cobalt of the same composition as the deposit are used as anodes. The pH of the electrolyte is of great importance, the optimum ranging from 5 to 7. The tungsten content of the deposit is 51% at a pH of 7. Lowering the pH by the addition of sulfuric acid reduces the tungsten content. At pH 6.1, 47%, at 5.8, 42%, and at 5.2 only 36% tungsten is deposited. The throwing power of the solution at a pH of 7.0 to 6.5 is excellent. It is lowered with a decrease in pH. A current efficiency of 30% is constant at a temperature between 80° and 102°C. Current efficiency is only 16% at 50°C. At temperatures near the boiling point, the deposits are bright and light. Lowering the temperature yields matte and dark coatings. For smooth deposits, a current density

of 1.5 to 2 amps./dm.^{2} is required. Alloy deposits of tungsten-cobalt were found to be considerable harder than pure tungsten. They resist hydrochloric, nitric, and sulfuric acids in all concentrations rather well and the resistivity is increased by a higher tungsten content. However, the coatings are not impervious and blacken rapidly when wetted. The crystalline structures of tungsten-iron, tungsten-cobalt, and tungsten-nickel alloys were found to be cubic body-centered, hexagonal, and cubic face-centered respectively.

This is an abstract by W. A. Willmann from an article by H. Offermanns and M. V. Stackelberg in the June, 1947, issue of "Metalloberflaeche", a German publication of recent origin.

Scientists Are Born That Way

Capacity for creative thinking is a relatively rare inborn talent. Under proper environmental stimulation, it develops that quality of mind essential in original research. Advances in science will depend upon discovering this talent and putting it to work. The need for doing this is well recognized to be in the national interest and is giving rise to the appropriation of vast federal funds for research and legislation toward the establishment of a National Science Foundation. These measures, valuable as they can be in encouraging the development of scientific ability, cannot create scientists. From the overcrowded graduate schools come hundreds each year with the doctorate in chemistry and other sciences. Yet the great majority of these young Ph.D.'s have no real ability in original thinking! Learned, proficient, and skilled they may be in experimental techniques, but these are not substitutes for intelligence and the capacity to have ideas.

It is evident that the first and most important step toward increasing the yield of men qualified for research is to seek out and recognize the essential talent when it appears. Graduate schools need to become more discriminating in their acceptance of candidates for the doctoral degree and more courageous in rejecting those lacking the qualification. Too often the persistent attain what only the gifted deserve. By the assignment of problems requiring the exercise of research talent early in the first year of graduate work, it should be possible to discern latent ability if it exists. Those who display definite evidence of research capacity should then be admitted to what might be called the "higher" graduate school and go on for the doctorate. The present emphasis in graduate training on course work and doctoral thesis often fails to allow sufficient opportunity for training in and practice of research methods. As a consequence, men enter research careers lacking familiarity with the research approach to problems.

It is not more graduate school capacity that is needed today but better selection of those who are to be trained. Men possessing capacity for creative thinking deserve the full attention of graduate faculties and school facilities. Society will be the beneficiary when this comes about.

R. M. B.

News Notes

THE LOCAL SECTIONS OF THE SOCIETY

WILLIAM CABLER MOORE, *Chairman*
Local Section Advisory Committee

From three in 1904, the number of local sections has grown to ten in 1948.

In the Society's youth, the problems of these sections were few and simple. Expenses were light, speakers were easy to get and there was relatively little competition for the attention of the members from other technical societies. In fact, in those early days the sections were largely autonomous, and only rarely referred any of their difficulties, including those of a financial nature, to the Board of Directors. On the other hand, the central management of the Society was inclined to look upon the local groups only as convenient hosts for one of the Society's semi-annual meetings and as agents for increasing the Society's membership.

However, with the passing years, the problems of the sections not only multiplied but soon became so pressing that they could be solved only by cooperation of the sections with each other and by careful, sympathetic action by the Board of Directors.

The first of these difficulties to be attacked was the financial one. In the administration of President Burns, not only were the regulations governing financial aid by the National Society to the local sections clarified and strengthened, but definite means for assuring section financial stability were indicated. The committee responsible for this forward action made several other suggestions practically all of which were incorporated into the By-Laws adopted in the spring of 1944.

One of the serious situations to which the national officers have given considerable thought for many years is the fact that hitherto no machinery existed by which the local sections could secure representation upon the Board of Directors without enlarging the Board to an unwieldy size. This difficulty was happily solved in the summer of 1947 when the Board authorized President Heise to request each section to name two delegates, one for a one-year term, the other for a two-year term, to a "Local Section Advisory Committee." The response to this invitation was gratifying, and this Committee held a two-hour session at the Boston meeting in October 1947, at which time many problems of vital importance to the sections were discussed. At the same time this section group was made a sub-committee of the Ways and Means Committee; and by the simple device of appointing the immediate Past President of the Society as chairman of this sub-committee, the sections for the first time in the history of the Society were assured of a voice in its management.

PROPOSED AMENDMENTS

Steps are now being taken to amend the Constitution and By-Laws of the Society to provide for the election by the Local Section Advisory Committee of its own chairman who will then automatically become a member of the Board. The members of the Society are urged to vote in favor of these changes when the matter is formally brought to their attention by the "mail vote" in the coming summer.

The modern viewpoint, of course, is that the sections and the National Society are mutually dependent on each other. The Society itself can aid the sections by suggesting methods of orderly procedure in the conduct of their affairs (including their financial aspects); by suggestions for speakers and through the Local Section Advisory Committee by sponsoring the discussion of problems of common interest to all the sections.

The sections themselves can aid each other by conscientious, accurate, and reliable reports on speakers who have appeared, or who want to appear on programs; by cooperation in arranging programs either on a regional basis or for the appearance on tour of desirable speakers; by suggestions as to proper methods of cooperation with other technical groups and by round-table discussions on topics of mutual interest at Advisory Committee meetings during national conventions.

Finally, local sections are assets to the National Society in that they may serve as hosts for national conventions; as try-out locations for speakers and for papers; as recruiting agents for the Membership Committee; and as training grounds for the men who will have to manage the Society's affairs in the future.

It is confidently expected that the strengthening of the bonds between the various sections, and between the sections and the Society, as provided for in the revised Constitution and By-Laws, will inaugurate a new era of growth and prosperity for the sections and for the Society as a whole.

DIVISION NEWS

Electric Insulation Division

M. C. Bloom, *Secretary-Treasurer*
324½ Beacon St.,
Boston, Mass.

The Electric Insulation Division has elected by ballot of Division membership the following new officers who assumed office January 1, 1948:

Dr. John F. Gall, *Chairman*
18 Schiller Ave.,
Narbeth, Pa.

Dr. Judson West, Jr., *Vice Chairman*
Magnavox Co., Inc.,
2131 Bueter Rd.,
Fort Wayne, Ind.

Mr. Mortimer C. Bloom, *Secretary-Treasurer*
324½ Beacon St.,
Boston, Mass.

Industrial Electrolytic Division

M. S. Kircher, *Secretary-Treasurer*
Booker Electrochemical Co.,
Niagara Falls, N. Y.

The Electrolytic Production of Metals Symposium, sponsored by the Industrial Electrolytic Division for the Fall Convention in New York, October, 1948, will present papers dealing with the following subjects:

Electrolytic Production of Manganese
European Aluminum Developments
Electrolytic Iron
Recovery of Silver from Used Photographic Emulsions
Theory of Aluminum Electrolysis
Influence of the Anion on Metal Deposition.

Several other papers are expected to complete the list which will be published later together with the authors' names.

The Nominating Committee of the Industrial Electrolytic Division, appointed at the Boston Convention, October, 1947, submit the following names of qualified nominees for officers of the Division:

R. E. Cushing, *Chairman*
Pennsylvania Salt Mfg. Co.,
Wyandotte, Mich.

R. B. MacMullin, *Vice Chairman*
8249 Troy Ave.,
Niagara Falls, N. Y.

M. S. Kircher, *Secretary-Treasurer*
Hooker Electrochemical Co.,
Niagara Falls, N. Y.

"At the election meeting during the spring convention, the report of nominating committee shall be presented after which additional nominations may be made from the floor by active members of this Division."

The attention of members is called to the following changes in the By-Laws of the Division.

In accordance with Article IX of the By-Laws of the Industrial Electrolytic Division, the following notice of proposed amendment in the By-Laws is announced. A vote will be taken on these proposed amendments at the annual meeting of the Division to be held during the spring 1948 Convention of the Society.

ARTICLE III—MEMBERSHIP—*at present reads as follows:*

"1. The active membership of the Industrial Electrolytic Division shall be those members in good standing of The Electrochemical Society who register with the Secretary of The Electrochemical Society their desire to be members of this Division and who pay Divisional dues as provided by these By-Laws.

2. The annual dues of this Division shall be fifty cents and shall be collected by the Treasurer of The Electrochemical Society, who shall turn them over to the Secretary-Treasurer of the Industrial Electrolytic Division."

It is proposed to change this to read as follows:

"1. The active membership of the Industrial Electrolytic Division shall be those members in good standing of The Electrochemical Society who register with the Secretary of The Electrochemical Society their desire to be members of this Division and who pay an initiation fee and Divisional dues as provided by these By-Laws.

"2. An initiation fee of $1.00, to be collected by the Treasurer of the Division, shall be payable by each member upon joining the Division effective May

1, 1948. The annual dues of this Division shall be fifty cents and shall be collected by the Treasurer of the Division. The Executive Committee at its discretion may waive assessment of dues in any year when the treasury is deemed to contain sufficient funds."

Based upon past experience the income from initiation fees should be adequate to meet the regular expenses of operating the Division. Hence normally no collection of dues will be necessary. However, it is believed desirable for the Division to retain the right to collect dues in case future events should make it desirable to do so.—M. S. Kircher, *Secretary-Treasurer*, Industrial Electrolytic Division.

SECTION NEWS

Niagara Falls Section

M. S. Kircher, *Secretary-Treasurer*
Hooker Electrochemical Co.,
Niagara Falls, N. Y.

Dr. A. L. Ferguson, Professor of Chemistry, University of Michigan, spoke on "Polarization and Overvoltage" at the January 14, 1948, meeting of the Niagara Falls Section at Red Coach Inn, Niagara Falls. The basic concepts and definitions involved in polarization and overvoltage, together with a brief reference to those electrochemical phenomena in which polarization and overvoltage play a prominent part were presented in a copiously illustrated lecture which was very effective.

The next meeting of the Section will be held jointly with the Western New York Section of the American Chemical Society on February 17, 1948, at Prospect House, Niagara Falls. Dr. George W. Heise, National Society President, will speak on "Some Applications of Porous Carbon Electrodes."

GEORGE A. PERLEY DISCUSSES GLASS ELECTRODE BEFORE PHILADELPHIA SECTION

J. F. Hazel, *Secretary*

Harrison Laboratory of Chemistry
34th and Spruce Streets
Philadelphia 4, Pa.

Fifty-five members and guests attended the dinner of the second meeting of the Philadelphia Section's 1947–48 season held in the Harrison Laboratory, University of Pennsylvania, January 8, 1948.

One hundred attended the address after the dinner which was delivered by Dr. George A. Perley on "Trends in the Development of Glass Electrodes." Chairman Cherry introduced the speaker who is a past chairman of the Philadelphia Section and is now in charge of the Chemical Division of the Research Department of Leeds and Northrup Company. Dr. Perley stressed the modern electrode in the development of which he has played an important part. The interesting demonstrations included the blowing of a glass electrode and its use for a pH measurement.

Dr. Perley came to Leeds and Northrup from the University of New Hampshire where he had been a chemistry professor for nineteen years. The experimental determination of pH has engaged his attention for the greater part of his career. He has been particularly interested in the glass electrode and has made noteworthy advances in this field. Dr. Perley stressed glass composition and other mechanical features of the electrode.

IMPRESSIONS OF ELECTROCHEMICAL INDUSTRY IN NORWAY DISCUSSED AT PITTSBURGH

Richard Rimbach, *Secretary*
1117 Wolfendale Street
Pittsburgh 12, Pa.

Dr. Earl A. Gulbransen of the Chemical Department, Westinghouse Electric Corporation Research Laboratories, delivered an especially interesting and illuminating talk on "Impressions of the Electrochemical Industry in Norway and the Paris Congress on the Corrosion of Metals" before the Pittsburgh Section on January 12, 1948.

During September and October, 1947, Dr. Gulbransen visited many electrical and electrochemical industries and many research laboratories in England, France, Holland, Norway, and Sweden. In Norway the Rjukan and Heröen plants of the Norsk Hydro Company afforded gracious hospitality at the plant guest houses where the Norwegian cooking was one of the memorable delights of the trip.

The Norsk Hydro Company is the largest electrochemical industry in Scandinavia and one of the largest in the world. It has the distinction of being the first company to produce fixed nitrogen on a commercial basis. Early plants were based on the Birkeland-Eyde proc-

ess, the first one, put in operation in 1905, was located at Notodden. Here powerful electric arcs were used to combine atmospheric nitrogen with oxygen to form nitric oxide. During recent years the arc process has been gradually displaced by the more efficient ammonia synthesis method. Hydrogen for ammonia synthesis is obtained by the electrolysis of water and nitrogen by the liquifaction and distillation of air.

PARIS CONGRESS

The Paris Congress on the Corrosion of Metals was held in the pleasant surroundings of the Maison de la Chimie and attracted over three hundred scientists from Europe, England, and America. In spite of present day difficulties in France, no effort was spared to entertain the foreign delegates and to see that their visit was an interesting and memorable one. Social events were free and transportation was often provided. Hospitality shown to the foreign visitors was greatly appreciated and will long be remembered by them.

Dr. Gulbransen graduated with honors from The State College of Washington, B.S. in Chemical Engineering. He obtained his Ph.D. in physical chemistry from the University of Pittsburgh. From 1934 to 1940 he taught chemistry at Tufts College, Medford, Mass. Since 1940 he has been with Westinghouse Research Laboratories engaged in fundamental research on the reactions of metals and alloys with oxidizing and reducing atmospheres.

Dr. Gulbransen is Chairman of the Pittsburgh Section of the Electrochemical Society and Chairman of the Pittsburgh Conference on Surface Reactions to be held the week of June 7, 1948, at Mellon Institute.

COLUMBUS CONVENTION

The forthcoming Columbus Convention is expected to draw considerable attendance and members are to be reminded that hotel reservations should be secured early. Plans for the social and business aspects of the meeting are well in advance and will be explicitly described in the program booklet, now in preparation.

The annual reception and banquet will be held on Thursday evening, April 15, the reception to commence at 7:00 P.M. and the banquet at 8:00 o'clock. At this time, Mr. Heise will deliver his Presidential Address and the awards of various prizes will be made. A luncheon has been planned, including a speaker, for the same day. On Friday, a buffet supper is scheduled with entertainment to follow.

In addition to the technical sessions and the annual business meeting, there will be meetings of the Board of Directors, Local Section Delegates, and various Divisions electing new officers.

FUTURE MEETINGS OF THE ELECTROCHEMICAL SOCIETY

Columbus, Apr. 14–17, 1948, Deshler-Wallick, C. L. Faust, *Chairman.*
New York, Oct. 13–16, 1948, Pennsylvania, K. G. Compton, *Chairman.*
Philadelphia, Apr. 13–16, 1949, Pending, Ernest G. Enck, *Chairman.*
Chicago, Oct. 12–15, 1949, LaSalle, Clifford Hampel, *Chairman.*
Buffalo, N. Y., Oct. 11–14, 1950, Statler.

Sessions on Corrosion, Electronics and Electrothermics will be held at the Spring Conventions. Sessions on Electro-Organics, Electrolytic Cells and Electrodeposition at the Fall Conventions.

MANUSCRIPTS FOR FALL MEETING

At this time, several papers scheduled for presentation at the New York Convention of the Society have been received and are being processed for publication. It may be expected that these papers will appear in early issues of Volume 94 of the Journal, beginning in July. All authors who contemplate submitting technical articles to the Society for publication next summer are requested to submit the material in accordance with "Instructions to Authors" as much in advance as possible. For a paper to be published before the New York meeting occurs the manuscript should be received within the next few weeks.

Symposia are planned on the topics of Electrodeposition, Electrolytic Production of Metals, and General and Theoretical Electrochemistry. Papers along these lines will receive earlier attention and greater assurance of publication.

NATIONAL ASSOCIATION OF CORROSION ENGINEERS

St. Louis Convention, April 5–8, 1948

The following list of technical sessions symposia to be held at the Jefferson Hotel, St. Louis, Missouri, April 5 to 8 inclusive by the National Association of Corrosion Engineers includes additions to those previously published: Cathodic

Protection, Chemical Industry, Communications, Electrical Industry, Gas Industry, General Industry, Oil Industry, Protective Coatings for Metals, Salt Water Corrosion, and Water Industry.

Professor Mars G. Fontana, Ohio State University, is Chairman of the Technical Program Committee for these sessions, and he is also a member of the National Association of Corrosion Engineers Board of Directors.

INSTRUCTIONS TO AUTHORS OF PAPERS

Authors should be as brief as is consistent with clarity, and must omit all material which can be regarded as familiar to specialists in the particular field. The manuscript should be headed by the title of the paper, the author's name and his business or university connection. The title should be as specific as possible and should convey the exact subject matter and scope of the paper. General titles should be avoided. An *Abstract*, limited to about 100 words in length, stating concisely the scope of the paper, and a brief summary of results, should form the opening paragraph. Next should follow a brief paragraph pointing out the main objective for undertaking the investigation, presenting briefly the historical, theoretical, or practical aspects of the problem.

Under the caption *Experimental*, concisely outline the apparatus, solutions, temperatures, and general conditions employed. Results should be summarized in either tables or curves, preferably the latter. Tables of data should be condensed as much as possible. Illustrations will be reduced to a maximem of 4½ in. x 7 in. and after reduction should have lettering approximately $\frac{1}{16}$ in. high. Original drawings in India ink on tracing cloth or white paper are ideal but sharp, black and white reproductions may be used. Curves may be drawn on coordinate paper ruled only in blue. Typewritten captions for title and figure number should be supplied on a separate sheet. Photographs must be of glossy type and mounted flat. Micrographs should be rectangular rather than circular to conserve space. Each should bear an explanatory title giving magnifications, etching medium, etc. To avoid reduction in size in reproduction, authors should indicate section of photograph or micrograph which they would like shown.

Units of Measurement:

Weights and measures are to be given in the metric system.

Milliliters (ml.) is preferable to cubic centimeters (cc.) for expressing volumes.

If the English or other systems are used, metric equivalent values are to be added in parentheses.

Solution concentrations are to be expressed in grams per liter in preference to ounces per gallon.

Corrosion rates should be expressed in milligrams per square decimeter per day (mdd). Pitting rate should be given in millimeters per specified time interval.

As regards the algebraic signs of potentials, zinc is negative as compared with copper, positive.

Sulfur should be spelled with "f" and not "ph".

The use of proprietary names, trademarks, and trade names should be avoided if possible. If used, these should be capitalized so that the owner's legal rights will not be jeopardized. If used, explanatory footnotes defining briefly the terms used are to be appended.

Literature and patent references are to be given in the style adopted by *Chemical Abstracts*. For example:

F. Freas, Trans. Electrochem. Soc., **40**, 109 (1921).

H. T. S. Britton, "Hydrogen Ions", Vol. 1, p. 309, D. Van Nostrand Co. New York (1943).

H. F. Weiss (To Wood Conversion Co.) U. S. Pat. 1,695,445, Dec. 18, 1928.

There should be a *Discussion of the Results* or a general statement of the *Conclusions* reached. Finally, all literature references should be listed at the end of the paper on a separate sheet.

Papers submitted for publication must be in triplicate to avoid reviewing delays. They should be typewritten, double-spaced, with 2-3 cm. margins. Address all communications to the Secretary of The Electrochemical Society, whose office is at 235 West 102nd Street, New York 25, New York.

The publication of papers is governed by the following paragraphs of Article V of the Society's By-Laws: (1st sentence of Section 3 and Sections 8, 9, 10, 11).

PUBLICATION OF THE CORROSION HANDBOOK

The *Corrosion Handbook* is now available. John Wiley & Sons, Inc., publishers, announced publication on February 15th. The retail catalogue price is $12.00. This price, although exceeding the original objective of the Editorial Advisory Board, applies to a book totalling 1225 pages, which is 50% larger than first planned, and reflects only partially the increased costs of production over the past two years.

The cost will be less to members of the Society. You have received from the Secretary of the Society the details of the special prepublication price arrangement with the publisher and full directions as to the proper procedure in ordering a copy from John Wiley & Sons, Inc., 440 Fourth Avenue, New York 16, N. Y.

Plans for publishing the *Corrosion Handbook* began with organization of the Corrosion Division at the Fall Meeting in 1942. This was followed by a petition to the Board of Directors of the Society for permission to undertake the project. The Board of Directors, presided over at that time by Dr. R. M. Burns, immediately gave approval and support. Dr. H. H. Uhlig, then of the Research Laboratory of General Electric Company, and now of the Corrosion Laboratory of Massachusetts Institute of Technology, was appointed Editor. An Editorial Advisory Board was appointed at the same time consisting of: Dr. R. M. Burns, Secretary of The Electrochemical Society, Bell Telephone Laboratories; Dr. U. R. Evans, Cambridge University, England; Mr. W. H. Finkeldey, Singmaster and Breyer; Mr. F. L. LaQue, The International Nickel Company, Inc.; Mr. R. J. McKay, The International Nickel Company, Inc.; Dr. R. B. Mears, Carnegie-Illinois Steel Corporation; Dr. F. N. Speller, Consultant; Mr. L. G. Vande Bogart, Crane Company; and Dr. G. H. Young, Mellon Institute. Various experts were enlisted to contribute the 143 chapters of the book.

The *Corrosion Handbook* is the only book of its kind. It brings together for the first time a comprehensive cross-section of scientific data and industrial experience, the scope of which includes modern corrosion theory, corrosion properties of metals and alloys at ordinary and elevated temperatures, corrosion protection, and corrosion testing. Some data have not been published previously. The book includes sections on choice of metals and alloys for specific corrosive media and atmospheres that are among the most extensive ever published. These compilations alone required two years' work of a committee representing the chemical and metallurgical industries. The glossary of terms used in corrosion was also a long-term effort of both the Editorial Advisory Board and Subcommittee V. of the American Coordinating Committee on Corrosion who prepared this list of definitions specifically for the *Handbook*. In addition to the above, the volume also contains general information, and tables of data frequently used by investigators in the field of corrosion. These together with many hundreds of recent literature references make the book a practical, convenient, authoritative reference.

Widespread interest in the *Handbook* was expressed from the very start. Orders or letters of inquiry have come from all parts of this country and Canada. Similar letters from England, Austria, and China point to an interest in and concern with corrosion problems in other countries as well, where economies in industry, and conservation of metal resources are also of major importance. The organization and publication of the book came at a difficult period attended by shortages and crowded schedules, so that the volume is available later than it would have been normally. The Editor and the publishers, on behalf of the Society, hope that the usefulness of the *Handbook* to the reader, and the quality of its information and composition will, in part, mitigate any inconvenience caused by the delay.

It has been arranged by the contributors to the *Corrosion Handbook*, the Editorial Advisory Board, and the Editor that all royalties from sale of the book will be turned over to the Society for use in supporting similar activities in the field of corrosion.

JAMES A. LEE

Presidential Candiate

James A. Lee joined The Electrochemical Society twenty years ago and has served in one capacity or another on the Board of Directors almost continually for the past fifteen years. He was a manager of the Society from 1939 to 1941, and Vice President from 1941 to

1943, and again from 1945 to April, 1948.

Mr. Lee has served on various committees over the years. Recently he has been Chairman of the Membership Committee, and Chairman of the Ways and Means Committee since its formation in the spring of 1946. It was this latter Committee that was charged with the responsibility of changing the set-up of the Secretary's office, moving it to new quarters, employing an Assistant Secretary and making arrangements for publication of the Journal of The Electrochemical Society. Also, he heads the Editorial Board which was appointed to establish policies for the guidance of the editors in selecting and handling material for the publication.

Mr. Lee is managing editor of Chemical Engineering, formerly Chemical and Metallurgical Engineering. In this position he has devoted considerable time to the collection of corrosion data and to the writing of numerous articles on this subject. Before joining the magazine's editorial staff in 1928 he had been with the Bell Telephone Laboratories, Western Electric Co., Citizens Gas Co. of Indianapolis, Federal Dyestuff and Chemical Co. and the Chemical Warfare Service.

He attended Washington and Lee University, Columbia University, and Massachusetts Institute of Technology.

JAMES A. LEE
Presidential Candidate

E. GIDEON WIDELL

Presidential Candidate

E. Gideon Widell at present serves the Society as Chairman of the Electronics Divisions. He became a member in July, 1930, and has been active in Society affairs ever since.

Born in St. Paul, Minnesota, July 21, 1890, he attended the University of Minnesota receiving the B.S. degree in 1917. He served in the first world war Chemical Warfare Service for two years following, and then received an M.S. degree in 1921 from Massachusetts Institute of Technology.

With Duncan MacRae also of our Society, Widell joined the research staff of the Westinghouse Lamp Division and became one of the first to work on the modern version of the oxide-coated electron emitter which is used in most radio receiving tubes at the present time.

In 1930, Mr. Widell became a member of the research staff of the Radio Corporation of America, Victor Division, Harrison, New Jersey, where he has continued his chemical and physical researches in electronics. He has been

E. GIDEON WIDELL
Presidential Candidate

granted many United States and foreign patents on electronic discharge devices.

RALPH MAURICE HUNTER
Vice-Presidential Candidate

Ralph M. Hunter became a member of the Society in 1922 and has served on many committees in the last ten years. He has been Vice Chairman and Chairman of the Industrial Electrolytic Division, member of the Acheson Medal and Perkin Medal Award Committees, and served on the Board of Directors and Ways and Means Committee. He is

RALPH M. HUNTER
Vice-Presidential Candidate

at present a member of the latter Committee.

Born in Philadelphia, Pa., August 18, 1896, Ralph Hunter received the B.S. degree in Chemical Engineering from Case School of Applied Science in 1918. He became associated with The Dow Chemical Company in 1918 where he has remained and is now manager of the Electrochemical Division.

At the close of the recent war he was a member of the Technical Industrial Intelligence Committee investigating and reporting on the German electrochemical industry.

Mr. Hunter is a member of the American Chemical Society, American Institute of Chemical Engineers, Sigma Xi, and Chairman, General Industry Symposium, National Association of Corrosion Engineers, 1948.

FRANCIS M. TURNER
Vice-Presidential Candidate

Francis M. Turner is a graduate of the University of Toronto where he continued his post-graduate work in physical chemistry under the late Dr. W. Lash Miller, a past President of the Electrochemical Society.

Mr. Turner's interests in literature and publishing were evident in 1916

FRANCIS M. TURNER
Vice-Presidential Candidate

when he joined the Chemical Catalog Company, Inc., as Technical Editor and became Vice President of that company in 1925 and President in 1928. He is now Vice President of its successor, the Reinhold Publishing Corporation.

He has been a member of this Society since 1913 and is the donor of the Turner Book Prize. He is a life member of the Chemists' Club, New York, and holds membership in the American Chemical Society and the Society of Chemical Industry. Other society memberships are the Army Ordnance Association, the Chairmanship of the Technical and Scientific Book Publishers Group of the American Book Publishers Council, Inc. He is Secretary and a Director of

The Associates of the University of Toronto, Inc., of New York.

HERBERT H. UHLIG
Vice-Presidential Candidate

Herbert H. Uhlig received the degree of Sc.B. in Chemistry from Brown University in 1929 and his Ph.D. in physical chemistry from Massachusetts Institute of Technology in 1932.

His work in the field of corrosion began in 1936 when he became research associate at Massachusetts Institute of Technology, in charge of the Corrosion

HERBERT H. UHLIG
Vice-Presidential Candidate

Laboratory then established to investigate the stainless steels.

In 1940, he became a member of the staff of the General Electric Research Laboratory at Schenectady, where he continued investigations in corrosion and related fields pertaining to metals. In 1946, he returned to Massachusetts Institute of Technology as Associate Professor of Metallurgy in charge of the Corrosion Laboratory.

Dr. Uhlig's principal researches have been in corrosion and electrochemistry with particular emphasis on fundamental studies of passivity and the chemical and metallurgical behavior of corrosion-resistant alloys. He is editor of the *Corrosion Handbook*, sponsored by The Electrochemical Society and written by several experts in the field.

He served on the Board of Directors of The Electrochemical Society from 1943 to 1945, was Chairman of the Corrosion Division from 1945 to 1946, and Chairman of the Gibson Island Corrosion Conference held in 1946.

WILLIAM W. WINSHIP
Candidate for Treasurer

William W. Winship has been unanimously nominated for the office of Treasurer of the Society. He has served in this capacity continuously since 1943 rendering throughout this period service and advice of great value to the Society. Realizing the results of his efforts, the Nominating Committee has seen fit to nominate this candidate again unopposed. Mr. Winship, an active member of the Society since 1918, is Manager of the Thermal Syndicate, Ltd., of New York.

1948 MARDEN PRIZE WINNER

Dr. John W. Marden has announced that Miss Virginia Swartz, of Illinois Wesleyan University, has been awarded the Marden Prize for 1948. The prize, a year's membership in the Society, is presented annually to the senior student at Illinois Wesleyan demonstrating the most promise in the chemical field. Miss Swartz, by virtue of outstanding effort and achievement in chemistry, was unanimously nominated by her instructors for the honor of the award.

CLARENCE W. BALKE AWARDED THE PERKIN MEDAL

The highest honor to an American chemist, the Perkin Medal, awarded annually by the Perkin Medal Committee of the Chemical Societies centered in New York, of which the Electrochemical Society is one, was presented by the American Section of the Society of Chemical Industry to Dr. Clarence W. Balke at a dinner meeting at the Hotel Commodore, New York, January 9, 1948.

Dr. Balke, a member of the Electrochemical Society since 1932, was born of German parents in Auburn, Ohio, March 29, 1880 and graduated from Oberlin College in 1900. He then came under the influence of W. A. Noyes, who had gone to the University of Illinois from

the Bureau of Standards to build a strong chemistry department. Later he studied under the guidance of another noted American chemist, Edgar Fahs Smith, and received the Ph.D. from University of Pennsylvania in 1905.

Professor B. S. Hopkins, University of Illinois, spoke on the "Personal Side of the Medalist" and Professor Colin G. Fink, recipient of the Perkin Medal in 1934, discussed Dr. Balke's scientific contributions to the knowledge of rare metals, especially the refractory metals. The ancient Egyptians were thoroughly skilled in smelting and refining the common metals 5000 years ago. The refractory metals, tantalum, columbium, titanium, and tungsten, did not lend themselves to ancient metallurgical methods. New chemical methods for the extraction of tantalum from its ores had to be devised.

Dr. Balke gave the medal address, "The Story of Tantalum." By 1921 relatively large ingots of ductile, malleable tantalum were produced. A replica of the original two gram bar of tantalum was exhibited together with a bar several feet in length, representing production today. During the war tantalum played a phenomenal rôle in bone surgery, skull repair, etc. It is described medically as "biologically acceptable" indicating that it is nonirrating to human tissues and is not attacked by body fluids. Incidentally, it is one of the few metals which is resistant to hydrochloric acid. A five million dollar plant was constructed by the Defense Research Corporation to provide the large quantities of tantalum needed by the Army and Navy during the last war. Tantalum "gauze" for tissue repair forms a stable structure around which new tissue cells grow and to which they may adhere. The metallic gauze remains in the body after it has served its purpose and causes no discomfort or irritation.

Other uses of tantalum during the recent war was in ultrahigh frequency tubes used in radar. In the early days of radio, tantalum found application in rectifiers. Commercially it is valuable in heat exchange systems and as the carbide in cutting tools. The carbides of the refractory metals are extremely hard. Incorporating tantalum carbide into tungsten carbide cutting tools improves the cutting edge.

Dr. Marston T. Bogert, second recipient of the Perkin Medal, 1908, awarded to a United States chemist for outstanding accomplishment, presented the forty-second impression of this Medal to Dr. Balke.

WILLIAM J. KROLL VISITS EUROPE

William J. Kroll, who has been in Europe since the fall of 1947 visiting France, England, and Holland, reports that general conditions are still very bad in Europe. "In all three there is too little coal and the universities are shut down two days a week to save fuel. Discipline in England is astonishing. All government institutions run on a minimum of coal." He adds that microscopic electric stoves, which at best can heat only the feet, are supplied to visitors' offices.

In Grenoble Dr. Kroll visited Professor L. Andrieux and says, "He showed me a splendid collection of inorganic compounds which he made by fusion electrolysis. He operates with a few amperes only, being without sufficient financial means, but his results are quite conclusive. He believes that the deposition voltage at the cathode of a mixed salt bath is that of an alloy and not that of a metal, when the affinities are fairly close together. I believe that Prof. Andrieux is one of the foremost specialists in the fused electrolyte field."

In Holland Dr. Kroll visited Professor Van Arkel and states that for 200 students government allocations are just about $5000 a year. As a result of the devastations of war he has practically nothing to work with, neither furnaces, nor testing apparatus of any kind. His whole library was confiscated.

Dr. Kroll has sold his metallurgical engineering laboratory in Luxembourg and most of the equipment, chiefly to the Institut de le Siderurgie, St. Germain en Laye, France, where, he states, there is a very vital need for all types of laboratory equipment and even the smallest quartz tube sells without effort. Dr. Kroll will return to America shortly.

GEORGE MAGRUDER BERRY

George Magruder Berry, prominent industrial metallurgist and chemist, died in Syracuse, New York, September 14, 1947. Mr. Berry was born in Maryland in 1878 and received a B.S. degree from George Washington University in 1899.

He was a member of The American Chemical Society, The Electrochemical Society, The American Institute of Min-

ing and Metallurgical Engineers, The American Society for Engineering Education, and The American Foundrymen's Association. Mr. Berry is survived by his wife, a son, George Magruder Berry, Jr., and a granddaughter.

PERSONALS

DR. COLIN G. FINK delivered the address on the scientific achievements of the medalist at the forty-second annual Perkin Medal award to Dr. Clarence W. Balke, January 9, 1948, in New York. The award is made by the Perkin Medal Committee of the Chemical Societies centered in New York, of which the Electrochemical Society is one, and was presented by the American Section of the Society of Chemical Industry. Dr. Fink will also visit the Midland and Chicago Sections on March 4 and 5 speaking on selected subjects from the thirty odd unsolved problems of electrochemistry.

JOHN KRUESI has advised that effective January 1, 1948, Tennessee Products & Chemical Corporation will operate the plant of Southern Ferro Alloys Company in Chattanooga, which it acquired in May, 1947, as its Southern Ferro Alloys Division. Mr. Kruesi will continue as Manager.

W. J. HAMER of the National Bureau of Standards received the distinguished honor of election to fellowship in the New York Academy of Science at the Academy's annual meeting in New York in December. The Academy is the fourth oldest in the country with more than 4,000 members. Among the 152 new fellows were 56 chemists and chemical engineers.

R. L. BALDWIN has retired as Sales Development Manager, Electrode Products, National Carbon Co., Inc., Niagara Falls, New York, and has moved to Orinda, California.

K. M. WIGHT, formerly with the Susquehanna Pipe Line Company, Philadelphia, Pa., is now connected with the National Cancer Institute, National Institute of Health, Bethesda, Maryland.

NICOLO ACQUISTA, formerly with Telecommunication Company, Brooklyn, New York, is now connected with the Radiometric and Infrared Section of the National Bureau of Standards, Washington, D. C.

ROBERT R. PIERCE of the Pennsylvania Salt Manufacturing Company and formerly located in Tacoma, Washington, is now stationed in Pennsauken, New Jersey.

F. R. MALLALIEU, Executive Engineer Telephone Division, Dictograph Products, Inc., formerly located at Oxford, Pennsylvania, now has headquarters in New York City.

THOMAS P. MAY, formerly connected with the United States Naval Research Laboratory, Washington, D. C., is now with the International Nickel Company, New York.

RALPH F. WEHRMANN is now with the Fansteel Metallurgical Corporation, North Chicago, Illinois.

BERNARD AGRUSS, formerly at Battelle Memorial Institute, Columbus, Ohio, has accepted a position in the Engineering Research Department, University of Michigan, Ann Arbor, Michigan, beginning February 1, 1948.

NATALIE GOLDOWSKI, formerly of Princeton, New Jersey, is now at Black Mountain College, Black Mountain, North Carolina.

MAX A. BREDIG, formerly with Monsanto Chemical Co., Knoxville, Tennessee, is now at Clinton National Laboratory, Oak Ridge, Tennessee.

DR. MARCELLO PIRANI has left Surrey, England, and is now residing in Glasgow, Scotland.

ROYCE H. LEROY, formerly of Bar-Rusto Plating Corporation, Kansas City, Missouri, is now Visiting Associate Professor of Chemistry, The University of Nebraska, Lincoln, Nebraska, while Professor H. G. Deming is on leave of absence teaching at the University of Hawaii.

POSITIONS AVAILABLE

ELECTROCHEMICAL ENGINEER thoroughly familiar with the manufacture and production of Dry Cell Flashlight Batteries to take charge of new manufacturing plant in Colombia, South America, the only battery manufacturing plant

in Colombia. Reply to Box A-199, Electrochemical Society, Inc., 235 West 102nd St., New York 25, N. Y.

POSITIONS WANTED

ELECTROCHEMIST, B. Chem., M. Chem., Physical Chemistry major Cornell University. Experienced in corrosion chemistry and all phases of metal finishing, electrochemical analysis, electrophoresis, organic and inorganic electrochemical preparations, fused salts, and as research group leader. Desires responsible executive position. Reply to Box 315, Electrochemical Society, Inc., 235 West 102nd St., New York 25, N. Y.

ELECTROCHEMIST, B.Sc., Ph.D. (London) desires position in America in Technical Sales and European Exports consultant. Exceptionally qualified technical executive, twelve years varied experience in research, product development, and consumer market research. Specialist in electroplating special alloys. Fluent French and German. Minimum remuneration $8000. Age 35, residing in London. Reply to Box 316, Electrochemical Society, Inc., 235 West 102nd St., New York 25, N. Y.

ELECTROCHEMIST, broad experience in research, development process control, industrial materials, engineering, and finishing methods. Metropolitan New York or New England area preferred. Reply to Box 317, Electrochemical Society, Inc., 235 West 102nd St., New York 25, N. Y.

CHEMICAL ENGINEER, Experienced in organic and inorganic metal finishing. Age 27. Seeks position in sales or research department of progressive firm. Reply to Box 318, Electrochemical Society, Inc., 235 West 102nd St., New York 25, N. Y.

NEW MEMBERS

At the meeting of the Executive Committee held on February 6, 1948, at the office of The Electrochemical Society, Inc., 235 West 102nd St., New York City, the following were elected to membership:

CARL A. AREND, JR., International Minerals and Chemical Corp., Columbia Park, Ohio (Alkali and Chlorine)

JOSEPH A. CALDWELL, Humble Oil & Refining Co.; 1052 Humble Bldg., Houston, Texas (Corrosion)

JOSÉ G. CASILLAS, Phillips Petroleum Co., Box 831, Bartlesville, Okla. (Theoretical Electrochemistry, Organic Electrochemistry, Electrodeposition, Alkali and Chlorine)

JOSEPH F. CERNESS, Cleveland Graphite Bronze Co., mailing add: 14507 Strathmore Ave., E. Cleveland 12, Ohio (Theoret. Electrochem., Electrodep., Electrothermics)

CARLO CIRIELLO, Giunta Tecnica de Gruppo Edison, Foro Bonaparte 31, Milano, Italy (Electrothermics, Power)

FARRINGTON DANIELS, University of Wisconsin, Chem. Bldg., Madison, Wisconsin (Theoret. Electrochem., Batteries)

EDWIN C. HALLIGAN, Ford Motor Co., mailing add: 10043 Aurora, Detroit 27, Michigan (Theoret. Electrochem., Electronics, Dielectrics)

DUDLEY H. HASKELL, W. P. Fuller and Co., So. San Francisco, California (Theoret. Electrochem., Batteries, Corrosion, Electronics, Dielectrics)

BENJAMIN P. HECHT, Sylvania Electric Products, Inc., mailing add: 112 Glenway St., Dorchester, Mass. (Theoret. Electrochem., Organic Electrochem., Electrodep., Electronics)

HAROLD WILLIAM GEORGE HIGNETT, The Mond Nickel Co. Ltd., D. & R. Lab., Wiggin St., Birmingham 16, England (Theoret. Electrochem., Batteries, Corrosion, Electrodep., Electrothermics, Electronics)

LOUIS KOENIG, Armour Research Foundation, mailing add: 35 W. 33rd St., Chicago 16, Ill. (Theoret. Electrochem., Batteries, Alkali and Chlorine, Electrodep.)

JOHN CHARLES McMULLEN, The Carborundum Co., Niagara Falls, N. Y. (Theoretical Electrochem., Corrosion, Power)

JAMES M. MOZLEY, JR., Washington University, Dept. of Chem. Engr., St. Louis 5, Missouri (Theoretical Electrochem., Organic Electrochem., Corrosion, Electronics, Dielectrics)

GEORGE W. MURPHY, University of Wisconsin, Dept. of Chem., Madison 6, Wisconsin (Theoretical Electrochemistry)

SUSANNAH ROWENA PYKE, National Research Council, Ottawa, Canada (Theoret. Electrochemistry, Corrosion)

JOHN F. RITTENHOUSE, C & D Batteries, Inc., Washington & Cherry Sts., Conshohocken, Pa. (Batteries)

HENRY G. ROEBKE, Texas Division, Dow Chem. Co., mailing add: 1323 W. 2nd Street, Freeport, Texas (Corrosion, Alkali and Chlorine)

JOHN RUSSELL, Research Laboratory, Eastman Kodak Co., Rochester, N. Y. (Theoretical Electrochemistry, Electronics)

ROBERT DONALD SCHWARTZ, Linde Air Products Co., mailing add: 120 Richmond Ave., Buffalo, N. Y. (Theoretical Electrochem., Corrosion, Electrodep.)

DHARAMDAS MANILAL SHAH, Estrela Batteries Ltd., mailing add: 33 Chowpatty Rd., Bombay, India (Theoret. Electrochem., Batteries, Corrosion, Electrodep.)

ARTHUR B. WINTRINGHAM, Ethyl Corp., mailing add: 1903 Blouin Ave., Baton Rouge, Louisiana (Alkali and Chlorine)

BROOKHAVEN NATIONAL LABORATORY ATOMIC ENERGY EXHIBIT

January 21–April 5, 1948

American Museum of Natural History

New York

A comprehensive exhibit on atomic energy, the largest of its kind in the country, opened January 21 at the American Museum of Natural History, Education Hall, for a two and one-half months' demonstration to the public of the beneficial applications of this most spectacular and strategic wartime development of theoretical and applied physics.

The exhibit is sponsored by Brookhaven National Laboratory on Long Island, nuclear research center of the Northeast, operated by Associated Universities, Inc., under auspices of the U. S. Atomic Energy Commission. Special group tours may be arranged through the Museum by organizations desiring to view the exhibit as part of their program activities during the period, January 21 to April 5, 1948.

The exhibit is open to the public during regular Museum hours and includes a demonstration of nuclear fission as it occurs in an atomic pile, with striking visual and sound effects caused by the actual disintegration of uranium atoms. The neutron source of this "model atomic pile" is radium-beryllium valued at $10,000.

Beneficial applications of nuclear energy are suggested by an "atomic power plant" which shows by special lighting effects how an atomic pile may be adapted to provide heat energy to drive electric turbo-generators. An animated "pin ball" panel shows the disintegration of U-235 atoms in a chain reaction. Radioactive isotopes used in medical, biological, and chemical investigations as "tracers" are dramatically illustrated by "Mr. Atom."

The basic principles of the rôles of atoms and subatomic particles as "building blocks" of matter, holding great potentials for energy production and other benefits, are explained by diagrams and panels. The national program of the U. S. Atomic Energy Commission showing the relationships of the national laboratories, such as Brookhaven, to the research facilities of their regions are portrayed. World sources of uranium and thorium ores, vital raw materials in the nuclear energy field, are identified by large maps and panels.

COMMENTS ON FURNACE PRACTICE IN WESTERN EUROPE

W. B. WALLIS, *President*

Pittsburgh Lectromelt Furnace Corp., Pittsburgh, Pa.

FERRO-ALLOYS

The use of electric energy for the making of ferro-alloys, insofar as Western Europe is concerned, is limited to Norway and Sweden, southeastern France and northern Italy, with new installations being made in Spain. During the war England installed plants for ferro-alloy production but these have been shut down since the war's termination, due to the shortage of coal and high power cost.

The use of electric energy for the reduction of concentrates and oxides has been limited to Norway, Sweden and northern Italy, with installations being made at present in northern Spain. Electric furnaces for the melting of metallics have been in use for many years in all of Western Europe.

In the ferro-alloy field, the new development, since the beginning of the war, has been the introduction of the rotating hearth or Elkem furnace in

Norway and Sweden. It is claimed for this furnace, due to the slow rotation of the hearth—usually around one revolution in 72 to 96 hours—that the furnace works much better on smelting and reduction work and that there is a tendency to reduce blows so that better thermal economies are had on smelting operations.

The writer visited only one of these installations—at Porsgrunn in Norway—a 10,000 kv.-amp. furnace operating on 75% ferro-silicon, and the management seemed to be well pleased with the furnace operation, feeling they were being repaid for their much larger investment over the older type smelting furnaces operating in the same plant.

Practically all of the ferro-alloy furnaces in operation in Europe are of the round type and, for the most part, are operated open top. In this country we have, in general, larger size furnaces than are customary in Europe on ferro-alloy work, 10,000 kv.-amp. being about the maximum at present installed.

SMELTING FURNACES

On smelting type furnaces, and taking up first the question of pig iron, the original design was built around the vertical shaft type as installed at Domnarvet in Sweden. This type furnace was superseded by the Tysland Hole furnace, the first of which, I believe, was installed at the Spigerwerk plant in Oslo in 1928. This was an oblong furnace with three electrodes in line, the furnace being roofed and use made of the gases generated in the operation.

These units usually ranged in size from 6000 to 12,000 kv.-amp. but are being superseded by much larger furnaces having capacities of 24,000 kv.-amp. Where this capacity is reached the electrical problems necessitate placing the electrodes in triangle formation and closing the delta at the electrodes in order to maintain good power factor where 50 cycle current is used.

The Swedish government, at the present time, is building a steel plant at Lulea in Sweden that will be equipped with three 24,000 kv.-amp. electric pig iron smelters of the circular type. The Norwegian government is planning an installation of two furnaces in a plant north of Narvik. These electric pig iron furnaces will feed metal to converters thence to duplexing electric furnaces for the finishing of steel.

Just what results are to be had with these large units in the national steel plants of Sweden and Norway remains to be seen but the writer observed at Domnarvet two 6000 kw, three-electrode, in-line furnaces operating on pig iron, the kilowatt hour consumption being 2000 per metric ton of pig and the electrode consumption 13 kg. per metric ton of electric pig iron produced.

The furnaces, as previously stated, are roofed and are spout charged from overhead bunkers so that they require but small crews for their operation. The manhours per metric ton of pig iron, for a furnace of around 6000 kw. load, is five, whereas on the large furnaces, such as 24,000 kw., the manhours on a single furnace installation is estimated at two per metric ton of pig iron produced.

The usual production on a 6000 kw. furnace is from 17,000 to 20,000 metric tons of pig iron per year while with the 24,000 kw. unit the estimated production is from 55,000 to 60,000 metric tons per year.

In the early days, charcoal was used as a reducing agent but, since the war, coke, coke breeze, and anthracite are being substituted with a slight increase in the kilowatt hour consumption per metric ton of pig iron produced, the general rule being that the higher the slag content of the reducing agent the higher the kilowatt hour consumption. Where coke is used instead of charcoal, the power consumption is usually increased from 4 to 5%.

The first electric pig iron furnace was of 6000 kv.-amp. capacity and rated at about fifty tons per day. It is reported that there are about sixteen furnaces of this size installed in the various countries mentioned. The only installations outside of Western Europe and northern Italy are in Japan, India, and Hungary. There have now been nine 12,000 kv.-amp. furnaces installed rated at 100 metric tons per day, the next step being the 24,000 kv.-amp. furnaces mentioned above.

Inasmuch as the usual operating power is 12,000 kv.-amp., we have to deal with currents up to 46,000 amp. per phase. When we step this up to 24,000 kv.-amp. we are getting into a current range that requires careful work in the secondary bus design and requires electrodes in triangle formation with the delta closed at the electrodes. Wherever possible, in Europe, they strive to supply furnaces of this size with twenty-five cycle power rather than fifty cycle power because of the power factor problems involved.

The alternate furnace type to this round design is to build a six-electrode furnace equivalent to three single phase furnaces in the same furnace tank and it was after this fashion that the 15,000 kv.-amp. furnaces at Petsamo, Finland were designed. These furnaces are used for the reduction of nickel from the sulfide concentrates and are the largest smelting furnaces of this type at present in operation. It is known that the Germans destroyed Petsamo on their retreat from northern Finland but the Russians have got the furnaces back into operation again.

There are no electric pig iron furnace installations in the western hemisphere although consideration has been and is being given to their installation in some of the South American countries and the western part of the United States.

MELTING FURNACES

Melting and refining furnaces were introduced into Europe on a commercial scale by Doctor Heroult in France and have come into vogue in almost every country. The percentage of electric steel produced in relation to total production is higher in Europe than in the United States. In the development of the electric furnace, they have, during the war, replaced most of the machine charged furnaces with top charge equipments and all new installations now being made or under contemplation are of the top charge design.

They have also designed a type of furnace which has the top charge feature and, in addition, has a rotatable hearth, the claims for this design being:

First, that a better melt-down of the cold scrap charge is obtained if the electrodes are worked through the scrap in one position; the electrodes then raised; the furnace rotated 60°; the power again turned on; the furnace then rotated back 120° and power turned on for the third time.

The second claim is made for the rotating hearth furnace during the refining period, the practice being to crack the roof slightly, or raise it above the shell, and then set the furnace hearth to rotating first 120° in one direction then back.

This equipment was introduced in Germany just prior to the war and a number of installations were made. The testimony of the users as to the results obtained is conflicting. In England and in Sweden statements were made that no faster refining was obtained due to the oscillation of the hearth although they felt that the ability to rotate the furnace, moving the position of the electrodes in relation to the scrap charge, was beneficial in melt-down. We believe this may be true where low voltages are used on melt-down. Most of the furnaces in Europe have a top melt-down voltage of about 200 v. or under.

In France, at a plant where there is one of these top charge, rotatable-hearth furnaces backed up by a substation of 275 v. melt-down, they feel that the rotation of the hearth is not beneficial on the melt-down but that better refining action is obtained. In Sweden, the statements were to the effect that no better refining was secured due to the rotating hearth.

No furnace of this design has been introduced to this hemisphere. In the first place, American practice has been to use higher powered electric furnaces than is customary in Europe and, secondly, we have used much higher melt down voltages than the Europeans. The recent practice of 380 v. melt-down, with installations going in at 480 v. melt-down, indicates the wide spread in the relative practices.

It is the opinion of the author that, with a proper melt-down voltage, no advantage is secured in varying the position of the electrodes in relation to the scrap charge by means of a rotatable hearth or by any other means. We, in this country, are getting clean, fast melting with the furnace hearth stationary, which is, after all, what is desired. The raising of the electrodes and the rotating of the hearth simply mean delay and lengthen the time of melt-down by the time required to perform these operations. From talks had with steel makers, it is doubted whether many more of these rotating hearth furnaces will be built in Europe.

Another practice that is peculiar to Sweden is that of placing an induction coil on the bottom of the shell and, after melt-down, turning on standard frequency power in that coil, setting up a stirring of the bath due to the inductive rotative action of the coil. This is a scheme proposed by the chief electrical company in Sweden and has its adherents within that country although we have yet to see any deep interest on the part of steel makers in other countries. We are, however, at the present time, building a furnace for a steel works in Sweden

to which this device will be applied and should, in due time, have a definite opinion based upon actual practice.

The type of top charge used in Europe is universally the old gantry type top charge where the roof is raised and the roof and superstructure traversed out over the ladle pit. We have had this type of top-charge furnace in use in the United States for many years, the first being the Ludlum Steel furnaces where the roof was raised and the furnace crucible traversed out from under the roof to permit top charging. Later, the American Bridge Company introduced top-charge furnaces here that are a replica of the Seimens top-charge furnaces in Europe. We originated the oil hydraulic roof-lift-swing type top-charge furnace and a number of this latter type are now being installed in Europe.

As to furnace capacities, European furnace ratings can be very misleading as they have some so-called twenty-five ton furnaces that are as large in physical dimensions as our eighty ton furnaces. They have for years, particularly on the Continent, used a practice of lining up the bottom and sidewalls with dolomite and using a depth of refractory bottoms up to 42 to 46 in. with the sidewalls tapering from 30 in. back to 24 in. at the top of the sidewall. This is in contrast to American practice where the depth of bottom refractories is held at from 16 to 18 in. and the sidewalls on the larger furnaces universally being 13½ in. in thickness.

The use of these very heavy rammed sidewalls results in the European steel maker discussing the heavier slag volumes that he is accustomed to using as compared with American practice. This condition is simply the result of the sluffing off of these heavy sidewalls during the making of the heat due to the fact that the refractories are set in with so great a thickness that there is no chance for a thermal balance to be set up.

With regard to automatic electrode controls, the Europeans were first to introduce the rotating type of control, which has come into vogue in this country within the past eight years. They do not have standardization of controls as we do. There are many varieties and types of furnace controls available in Europe, the only one which has striking merit is the rotating type control. They have not gone in for air blast circuit breakers as developed in this country, but have been adhering to the old line oil breaker as the standard.

The European engineer has been accustomed to using higher primary voltages on transformers than we have and has had more experience using high voltages on the primary. Not long ago our electrical manufacturers refused to quote on a furnace transformer for single step transformation of from 33 kv. down to furnace voltage. At the time that position was taken we had furnace transformers in operation in Europe of 36 kv. line voltage down to furnace voltage in a single step. Since that time there have been a number of 33 kv. installations made in this country and one 44 kv. but that appears to be the ceiling of engineering, whereas in Europe there are one or two installations of 50 kv. down to furnace voltage in a single step.

Another field in which our ceiling of engineering appears to be lower than that in Europe is in the matter of tap changers. We have had, for a number of years, very efficient off-load tap changers for furnace work whereas in Europe the design has gone forward on the basis of on-load tap changing. The author remembers in 1926 seeing an on-load tap changer installation for Germany and was impressed with the fact that the on-load tap changer was of physical size almost equal to that of the transformer itself. In 1947 the on-load tap changer had been engineered to the point that it was actually smaller than the off-load tap changers that are being designed and built by our electrical manufacturers.

There are two schools of thought as to the need for on-load tap changers for furnace work and, from a practical standpoint, it does seem to be a waste of money to buy that type of equipment for furnace work where voltage changes are made only once or twice during a heat. It seems especially foolish to install on-load tap changers on smelting work where a voltage change may not be made in six months. However, the author has observed a number of on-load tap changers on furnaces of this latter type. The point seems to be that the tool has been developed and the cost of its manufacture is no greater than that of an off-load tap changer. We, today, are in the position of not having perfected the designs, or at least not having had a great deal of experience with them, and, from an economical standpoint, the resultant prices of on-load tap changers in this country are almost prohibitive

as compared with the price of the off-load tap changer.

ELECTRODES

For ferro-alloy work and for smelting furnaces, the Soderberg or self-baking electrode is universally used throughout Europe whereas, in this country, we have relatively few installations of self-baking electrodes in these fields. The reasons, of course, are; first, the limit of size of graphite electrodes manufactured in Europe at the present time is in the neighborhood of 14 in. in diameter while we have 24 in. diameter graphite electrodes available; second, the quality of the European electrodes, due to the lack of proper raw materials, is markedly lower than that of the American graphite electrode. This is evidenced by the comparison of the American imported electrodes in operation in a plant along side of electrodes manufactured in Europe.

Recently there have been some very bad explosions of Soderberg electrodes in plants in Scandinavia, killing a number of men, and investigation is now under way to determine the cause. Indications are that the difficulty lies in the use of wood tar as a binder although the evidence is not at all conclusive.

The self-baking electrode is also used in a number of plants operating melting furnaces—chiefly in Sweden. The universal preference of the operator is for a graphite electrode where it can be obtained but for reasons of cost, non-availability, or bad quality of electrodes, the pre-formed electrode has not come into vogue in Europe as it has in this hemisphere where we do not have a single instance of a tilting type furnace utilizing self-baking electrodes.

FUTURE DEVELOPMENTS

In Norway and Sweden the national governments are taking steps to build electric steel plants starting with electric pig iron furnaces and will have productive capacities almost equal to the normal steel requirements of those countries.

In Belgium, Luxembourg and France there will be a number of electric furnace installations in place of equipment badly damaged or totally destroyed during the war.

In Spain there is a remarkable program afoot for the expansion of the steel industry due to the fact that Spain has been cut off from normal contacts with France and the balance of Europe. This planning is electric furnace-wise and is based upon a government program of development of water power in northern Spain.

Granted a reasonable period of peace, the next ten years should see Europe returning to a position where the percentage of electric furnace steel is as great as that prior to the war and, in a number of countries, in excess of that prior to the war. This statement is limited to those countries where the governments are planning increased water power developments.

PATENTS OF INTEREST TO ELECTROCHEMISTS

Selected by Fred. W. Dodson, Chairman of the Patent Committee, from the Official Gazette

December 23, 1947

Hayes, R. F.—2,433,047, Photopolymerization

Forbes, D. D.—2,433,209, Bus Bar Connector

Gleave, W. W.—2,433,212, Electrode for Use in Electrolytic Cells

Herzog, C.—2,433,218, Cold Cathode Fluorescent Lamp

December 30, 1947

McLarn, E. S.—2,433,384, Method of Manufacturing Unitary Multiple Connections

Saslaw, O.—2,433,401, Selenium Paste and Method of Making and Applying it

Saslaw, O.—2,433,402, Selenium Cell and Lacquer therefor

Smith, C. G.—2,433,404, Light Generating Device

Davidoff, C.—2,433,441, Electrolytic Production of Thin Metal Foil

Jarrett, T. C. and Guerke, R. D.—2,433,457, Chrome Plated Wear Resisting Surface

Vogel, P. C.—2,433,495, Tilting Induction Furnace with Leads extending through a Trunnion

Lamb, A. H.—2,433,566, Process for Manufacturing Photoelectric Cells of the Dry Disk Type

Solomon, M., deceased, by Solomon, N. W., administratrix—2,433,632, Fibrous Sheet Material for the Electrolytic Formation of Azo Dye Image Records thereon

Clapp, R. H.—2,433,809, Crater Lamp

Toorks, W. P.—2,433,821, Electron Emissive Cathode

January 6, 1948

Sutherland, B. P.; Thompson, J. B.; Simpkinson, C. H.; and Morris, D. D.

—2,433,871, Electrolytic Production of Hydrogen and Oxygen
Hansen, H. J.—2,433,989, Means for Automatically Supplying Distilled Water to Storage Batteries
Benner, H. L., and Bair, R. R.—2,434,191, Removing Organic Impurities from Copper-Cyanide Electroplating Baths

January 13, 1948

Pfann, W. G.—2,434,286, Method of Forming a Point at the end of a Wire
Schutte, H. S.—2,434,290, Electrolytic Tin Plate
Wise, E. M.—2,434,305, Electric Contact
Chace, P. G.—2,434,392, Thermostatic Element
Daellenbach, R. E.—2,434,398, Auto-Battery Terminal Connection
Kugler, H. W.—2,434,417, Small Parts Holder for Electrolytic Baths

January 20, 1948

Koppelman, M. D.—2,434,703, Dry Cell Closure
zu Eltz, A. E.—2,434,731, Platinum Sheet Electrode
Ross, J.; Potter, D. J.; and Yolles, S.—2,434,746, Process of Preparing Organic Sulphonic Derivatives
Froelich, H. C., and Hersey, A. R.—2,434,764, Calcium Cadmium Molybdate Phosphor
Kosterlitzky, J. L. T.—2,434,855, Process of Coating Metal Articles

ELECTROCHEMICAL ABSTRACTS PUBLISHED BY THE AMERICAN CHEMICAL SOCIETY

Dr. E. J. Crane, Editor of CHEMICAL ABSTRACTS, reports that the total number of electrochemical abstracts published in 1947 amounted to 498 as compared with 434 in 1946.

A.I.E.E. PUBLISHES USEFUL PAMPHLET

The American Institute of Electrical Engineers, 33 West 39th Street, New York 18, N. Y. has just published a thirty-three page pamphlet, copies of which are available to our members upon application to the American Institute of Electrical Engineers headquarters, attention: C. C. Wilson.

The pamphlet was sponsored by the American Institute of Electrical Engineers, in particular its committees on electrochemistry, electrometallurgy and electronics. The authors cover power converters and the broad aspects of the use of modern mercury arc rectifier conversion equipment in the zinc, magnesium, chlorine, aluminum, copper and the mining and smelting industries.

The various parts of this publication complement one another in that they show the common problems and practices encountered in the various industries in the use of this relatively new instrument for the conversion of very large amounts of power (up to an aggregate of 14 billion kilowatt-hours per year).

Methods of installation, maintenance and operation, discussed by engineers active in their own field, make this an important contribution to the understanding and use of large conversion apparatus.

Sustaining Members Are Essential

Sustaining membership provides an opportunity for industry to give financial support to technical societies covering their fields of interest. Without assistance from this source, it has proved difficult for relatively small societies in specialized fields to thrive; income from ordinary memberships does not meet the minimum cost of operation of a business and editorial office even though officers of such societies do not receive compensation. In consequence, affairs lag, routines must be performed by men busy in their normal occupations and by part-time clerical help, the volume and quality of technical papers fall off, and conventions lose their attractions.

The Electrochemical Society, with about 2500 members, is in these days a small society. During its nearly half century of existence, however, it has contributed notably to the advancement of the science and technology of electrochemistry. The semi-annual conventions of the Society provide opportunity for exhaustive discussion of technical subjects and intimate personal contact with fellow-scientists and engineers. By means of symposia, the nine Divisions of the Society achieve stimulating and effective treatment of their areas of specialization. With the establishment of the monthly Journal and the continuation of the Transactions, the Society provides prompt and adequate publication.

In no small degree the Society owes its present vigor to the financial assistance provided by its Sustaining Members. This additional support has meant the difference between bare existence or even extinction and the high level of activity which characterizes the Society today. It has also made it possible to employ an able, full-time office and publication manager and to furnish him with adequate clerical and editorial assistance, and finally to rent office quarters when it was no longer feasible to accept the generous hospitality of a well known university.

The cost of sustaining membership is small compared to the benefit derived by industrial concerns from the Society's meetings and publications which are devoted so intimately to their scientific and technologic interests. The management and the members of the Society appreciate the generous support which has been electrochemical industry's affirmative response. Nevertheless, there remains an urgent need for enlarging the list of sustaining members in order that the Society's future be assured should periods of business or economic depression occur. Members of the Society can be of assistance in the campaign for enlisting this additional support by calling attention to the advantages and benefits of Sustaining Membership.

R. M. B.

News Notes

BATTERY SYMPOSIUM IN CHICAGO

U. B. THOMAS

Dry cells made with magnesium instead of zinc, others which operate at 275°–400°F., 250-ampere flash currents from flashlight-size batteries, an electrolysis of water in which the yield is all oxygen and no hydrogen, miniature 18-volt storage batteries vacuum-packed in "Spam" cans.—These were some of the novelties described at the Battery Symposium at the Chicago Engineers Club on February 7 sponsored by the Chicago Section and the Battery Division of the Electrochemical Society. More than 125 members and guests were registered for a program which included thirteen papers on a wide variety of battery subjects. The feature of the all-day meeting was the luncheon at which President Heise addressed the group on the history and future prospects for cells using gas-depolarized electrodes.

All the arrangements for this highly successful meeting were handled by a committee composed of the officers of the Chicago Section, J. B. Mullen, J. H. Smith, R. B. Wittenberg, B. F. Freeberg; and C. A. Hampel, Program Committee Chairman, C. A. Crowley and O. W. Storey, Technical Program Chairman.

Morning Session

The morning session, presided over by Upton B. Thomas, opened with "A Survey of Voltaic Cells" presented by Morgan Sparks, Bell Telephone Laboratories. Chiefly historical, this paper traced the development of voltaic cells, both primary and secondary, from the early experiments of Volta through many stages to the modern commercial cells and mentioned briefly some of the specialized development work during the war. Dr. Sparks emphasized the electrochemical reactions involved rather than mechanical features of construction.

George W. Vinal, of the National Bureau of Standards and Chairman of the Society's Battery Division, presented "Standard Cells and the Change from International to Absolute Units." The paper, appearing in the technical section of this Journal, reviews briefly the development of standards of electrical units during the past century and indicates why a change is being made at this time.

Following Dr. Vinal's paper, R. C. Kirk described some of the recent work of the Dow Chemical Company in "Latest Developments in the Use of Magnesium in Batteries" by Mr. Kirk and A. B. Fry. Magnesium batteries are of great interest because of limitations of zinc resources and because magnesium has large theoretical advantages with respect to voltage and ampere-hour capacity per unit weight. The current work on dry cells, sponsored by the Signal Corps, is directed toward commercial as well as military uses and has as its aim the provision of fundamental data for use by battery manufacturers. The dry cells studied thus far are patterned after the Leclanché cell and these were demonstrated by Mr. Kirk in an ordinary flashlight. The best cells to date use a magnesium-alloy anode, MnO_2 and acetylene-black cathode, and a strontium bromide electrolyte, inhibited with ammonium chromate. These cells have initial capacities at 70°F. as good as the best commercial zinc dry cells and capacities at 0°F. which are superior to those of zinc cells. Magnesium cells have been stored eight months with as good a voltage as zinc cells after a similar period and excellent capacities have been attained after three months storage. Although magnesium has an initial advantage of 0.5 v. as compared with zinc, this advantage is lost during storage or in the initial stages of discharge. Future work will be directed primarily toward eliminating these voltage losses.

Four designs of the now familiar RM cell using zinc and mercuric oxide in caustic potash were described in "The Electrical Characteristics of the Ruben Cell" by Maurice Friedman of P. R. Mallory and Company, and Charles E. McCauley of Jersey City Junior College. Dr. Friedman also presented data showing the remarkable ability of these cells to withstand temperatures higher than are usually considered feasible for batteries. Cells stored at 55°C. (131°F.) for a year still delivered 70% of their theoretical capacity. RM cells have

been finding wide use in geophysical applications in which they are kept at temperatures of 135°C. (275°F.) for as long as 16 hours before use. Even under these severe conditions theoretical capacity is nearly realized. Miniature "button-type" cells, using a gel electrolyte, have been developed for small B batteries. A cylindrical cell $\frac{3}{8}$" (1.55 cm) in diameter by $\frac{7}{8}$" (4.7 cm) long, still in the experimental stage, will deliver steady currents of 0.2 ampere for 16 hours.

The final paper of the morning session was "The History of the Developmens of the RM Cell" by Grenville B. Ellis and Arthur F. Daniel, Signal Corpt Engineering Laboratories. Mr. Daniel reviewed the project from the earliest

Courtesy of Chem. and Eng. News

John Mullen, Chairman Chicago Section, introducing President Heise

contacts with the Ruben Laboratories in 1942 to the establishment, at the end of the war, of three large plants for the manufacture of RM batteries. Although the cell in its present stage of development cannot be considered a cure-all for military battery problems, its future in this field seems bright. Because of its high capacity per unit of weight and volume, it is promising for the miniaturization necessary in highly portable military equipment. Among the newer developments hinted at by Mr. Daniel are RM cells which operate efficiently at −65°F. and others, no larger than a D-size flashlight cell, capable of delivering flash currents of 250 amperes.

Luncheon Address

George W. Heise, long associated with the forward-looking research of the National Carbon Company, particularly in connection with the air-depolarized cell, was the featured speaker at luncheon. After being introduced by John B. Mullen, Chairman of the Chicago Section, Mr. Heise spoke on gas-depolarized electrodes, their past history and possible future. Electrodes of this type, though directly foreshadowed by the Grove hydrogen-oxygen cell of 1839, developed independently of that invention largely as the result of efforts to overcome hydrogen polarization in simple galvanic cells. Mr. Heise showed pictures from the patent literature indicating the remarkable lengths to which some inventors had gone in the direction of mechanical as well as chemical depolarization by brushing, agitation and aeration. The discovery that carbon "catalyzed" by very small additions of platinum, copper, silver and the like would make oxygen electrochemically active was followed in due course by the development of air-depolarized porous carbons capable of operating at current densities up to 6–10 amperes per square foot in modern primary batteries (e.g. the Zn:NaOH:C air-depolarized cell).

Mr. Heise explained further that, under proper conditions, oxygen electrodes can be made to function at more than 100 amperes per square foot. In this way they can be used in electrolyses where they can prevent hydrogen formation and, by lowering cell voltage, reduce power requirements. With air-breathing cathodes it is possible to bring about cathodic oxidation and to produce hydrogen peroxide at the cathode. Thus a cell can be devised to yield two equivalents of oxygen and no hydrogen per Faraday of current. This was described as "electro-winning" oxygen from the air. Since other gaseous depolarizers such as hydrogen, sulfur dioxide, or chlorine can also be used at carbon electrodes (though some require catalysts), the gas electrode seems capable of playing an important part in the future of electrochemistry.

Primary Cells

The afternoon session on Primary Cells, presided over by N. C. Cahoon, was opened by Professor P. W. Selwood of Northwestern University with "Structure Studies on MnO_2 and Related Compounds." Professor Selwood has proposed an interesting new method for studying the valence change of manganese during the discharge of a Leclanché dry cell by following changes in magnetic susceptibility. In preliminary investigations of this problem, the author made

the discovery that pyrolytic decomposition of $Mn(NO_3)_2$ gives Mn_2O_3 when supported on γ-Al_2O_3 and MnO_2 on rutile (rhombic TiO_2). In each case, the product is of the same crystal form as the substrate. This phenomenon was also observed in the pyrolysis of $Ni(NO_3)_2$.

G. H. Kissin and J. S. Carruthers, of the Georgia School of Technology, in their paper, "Progress Report on Investigation of the Electrochemical Production of MnO_2 for use in Dry Batteries," discussed the limitations of the classical method of producing high capacity battery ore by the electrolysis of hot acidified $MnSO_4$ solutions when employing graphite anodes. At high current densities, current efficiencies are low and graphite anodes suffer severe attack. By the use of platinum-clad anodes, it was possible to increase greatly the current efficiency at high current densities. The work, which is sponsored by the U. S. Army Signal Corps, is being extended to a semi pilot-plant scale.

The application of the electron microscope to the study of the structure of dry cell materials was demonstrated in the next paper, "Observations of Carbon Crystallites in Electron Micrographs" by G. Benson and J. D. Boadway of Shawinigan Chemicals Limited. Mr. Boadway showed electron micrographs of various carbon blacks which are interpreted as demonstrating the existence of carbon crystallites as small as 50Å. Both bright-field and dark-field micrographs were shown. Crystal dimensions agree with those obtained by X-ray diffraction.

The closing paper of the primary cell session was "Operation of Silver Chloride-Magnesium Batteries at Elevated Temperatures" by I. C. Blake and J. B. Mullen of Burgess Battery Company. By the use of a high-boiling electrolyte composed of 40% diethylene glycol and 60% water, it is possible to construct low voltage batteries which will operate for long periods at temperatures above the boiling point of water. In certain cases, satisfactory performance was obtained with ambient temperatures as high as 400°F. Although the high-temperature electrolyte is useful for many applications, service is limited in many respects. At high currents there is appreciable loss of capacity as the temperature is increased and high-voltage B batteries offer special problems above 250°F.

Secondary Cells

Mr. C. C. Rose presided over the session devoted to secondary cells. The first paper of this session, "The Discharge Process of the Storage Battery," was presented by Eugene F. Willihnganz of the National Battery Company. Dr. Willihnganz presented data which broke down the total cell potentials on charge, discharge and open circuit into their component parts: equilibrium potential of each electrode, various resistance drops, and individual electrode polarizations. With particular reference to the latter, it was shown that the negative plate polarizations can be explained in terms of the concentration of lead ions in solution in the immediate neighborhood of the lead surface. Particularly at high rates of discharge and at low temperatures, there is evidence of very considerable supersaturation of the electrolyte with lead sulfate. This condition is locally relieved by the very abrupt appearance of crystals of lead sulfate. This phenomenon was observed microscopically on specially designed cells. Potential changes take place on the positive which cannot be explained entirely on so simple a basis. Dr. Willihnganz proposed a detailed study of positive electrode behavior as a fruitful field for university research.

H. C. Riggs of the Electric Storage Battery Company followed with "Low Temperature Performance of Storage Batteries," which dealt particularly with aircraft engine starting problems. Mr. Riggs emphasized the gain in efficiency to be realized from a careful matching of battery and starter-motor characteristics. He further stated that, in general, it was more practical to keep a starting battery warm than to design one to operate at extremely low temperatures since it is practically impossible to charge a very cold battery. For example, a battery insulated with one inch of Celotex can be maintained 50°F. above the ambient temperature with an input to the heater of 40 watts. Low-temperature performance curves were given which show the practicability of predicting very low temperature performance from data obtained at two higher temperatures. This would simplify the routine testing of batteries by manufacturers.

Upton B. Thomas of Bell Telephone Laboratories presented a brief paper en-

titled "The Determination of the Efficiency of Storage Battery Vent Plugs." A method was described for absorbing the acid spray given off from batteries on overcharge and it was shown that a standard commercial vent plug removes all but 0.01% of the acid spray which would otherwise escape from the cell when overcharged at its normal rate.

The final paper of the session, "Construction and Performance of Plastic-Container, Electrolyte-Retaining Lead-Acid Batteries" by C. H. Endress and C. C. Rose, Willard Storage Battery Company, was given by Mr. Endress. In response to the demand for light-weight, non-spill storage batteries for portable radio sets, the Willard Company in 1940 undertook a development which reached very large scale production of a wide variety of designs for war purposes. Molded polystyrene was used for all cases and covers. Electrolyte-retaining separators were made from redwood bark fibre, treated and processed by a regular paper-making technique. Grids in a wide variety of shapes and sizes were cast in multiple so that they could be processed on regular production line equipment. Some of the smallest cells were assembled into A and B battery packs which were sealed in vacuum in lead-plated "Spam" cans. An ingenious device was used to puncture the can and admit acid to the battery. Sample batteries of many of the types developed were on display.

Since the Symposium was of an informal nature, no copies of the papers presented are available to the Society for distribution. Those who may be interested in more details of the various papers are requested to address their inquiries directly to the authors of the papers concerned. It is hoped that several of the studies described here will be formally presented at the Fall Meeting of the Society in New York where there will be a Technical Session devoted to battery papers. Those given in New York will, of course, be published in the Journal and the Transactions of the Society.

DIVISION NEWS

Industrial Electrolytic Division

M. S. Kircher, *Secretary-Treasurer*
Hooker Electrochemical Company
Niagara Falls, New York

As was mentioned in the March Journal, the attention of members is called to the following changes in the By-Laws of the Division.

In accordance with Article IX of the By-Laws of the Industrial Electrolytic Division, the following notice of proposed amendment in the By-Laws is announced. A vote will be taken on these proposed amendments at the annual meeting of the Division to be held during the spring 1948 Convention of the Society.

ARTICLE III—MEMBERSHIP—*at present reads as follows:*

"1. The active membership of the Industrial Electrolytic Division shall be those members in good standing of The Electrochemical Society who register with the Secretary of The Electrochemical Society their desire to be members of this Division and who pay Divisional dues as provided by these By-Laws.

"2. The annual dues of this Division shall be fifty cents and shall be collected by the Treasurer of The Electrochemical Society, who shall turn them over to the Secretary-Treasurer of the Industrial Electrolytic Division."

It is proposed to change this to read as follows:

"1. The active membership of the Industrial Electrolytic Division shall be those members in good standing of The Electrochemical Society who register with the Secretary of The Electrochemical Society their desire to be members of this Division and who pay an initiation fee and Divisional dues as provided by these By-Laws.

"2. An initiation fee of $1.00, to be collected by the Treasurer of the Division, shall be payable by each member upon joining the Division effective May 1, 1948. The annual dues of the Division shall be fifty cents and shall be collected by the Treasurer of the Division. The Executive Committee at its discretion may waive assessment of dues in any year when the treasury is deemed to contain sufficient funds."

Based upon past experience the income from initiation fees should be adequate to meet the regular expenses of operating the Division. Hence normally no collection of dues will be necessary. However, it is believed desirable for the Division to retain the right to collect dues in case future events should make it desirable to do so.

SECTION NEWS

Cleveland Section

Charles Sanborn, *Secretary-Treasurer*
2231 Wrenford Road
University Heights 18, Ohio

The initial 1948 meeting of the Cleveland Section was held at the Hotel Carter in Cleveland on January 13th. At this time, the guest speaker, President Heise, discussed "Applications of Gas-Depolarized Electrodes." (See Battery Symposium)

The Section met again on February 10th at the Carter. The guest speaker, Mr. W. M. Farnsworth of Republic Steel Corporation, gave a talk on "Electric Arc Furnace Practice." Mr. Farnsworth first discussed schemes and mechanical devices associated with the early history of electrically refined steel. He then described the standard large furnace of today which has a 20 foot diameter shell, a holding capacity of 170,000 to 180,000 pounds, is equipped with a 12,000 or 15,000 KVA transformer, and uses 20 inch graphite electrodes.

A furnace may be lined with either basic or acid materials. Because of greater flexibility, basic lining is used for the production of ingots. The basic hearth is lined with magnesite or dolomite and permits lime slags to be formed for the removal of sulfur and phosphorous. Acid practice is used largely in the production of steel castings.

The raw materials include scrap, ferro alloys, oxidizing agents, carburizers, and slag-forming materials. Scrap forms the bulk of charge and, due to the many types of alloy, stainless, and carbon steels produced, it is important that the various types be carefully segregated according to analysis. The scrap charge should be selected so that when melted it will contain only the elements desired in the steel to be produced.

In the production of various types of electric furnace quality alloy steel, two-slag practice is generally used and differs from the above only with regard to additions of alloys and deoxidizers. The lime and ore added during charging and melting form the oxidizing slag. The reaction between the carbon in the metal and the iron oxide creates a vigorous boil oxidizing the carbon; phosphorous and other oxidizable elements such as silicon, manganese, and chromium react to form oxides and revert to the slag. A high lime-silica ratio is desirable in the oxidizing slag and is controlled by the amount of lime added. The iron oxide content of the slag is important and a vigorous boiling action insures low hydrogen content and freedom from excessive non-metallic inclusions. These factors can be closely controlled in the electric furnace.

After the oxidizing reactions have taken place, the slag is removed and replaced with a deoxidizing slag composed of lime fluor spar, silica sand, and crushed coke. The fluor spar and sand assist fluidity and the coke, when fused with the lime, forms calcium carbide which reacts to remove the dissolved oxides from the bath and eliminate sulfur. Alloying additions are made and the heat is finished in the furnace under reducing conditions.

A great aid in temperature control is the recently developed emersion thermocouple for taking temperatures of the molten bath.

The electric furnace is particularly adaptable to the production of low carbon stainless and heat resistant steels. The major portion of stainless produced is under 0.12 carbon and a large tonnage of the 18-8 austenitic types are produced with a carbon limit of 0.07 maximum. Because of this low carbon limit, silicon is used as a reducing agent in place of crushed coke in the finishing slag.

Stainless steels have a high affinity for hydrogen at melting temperatures. When an appreciable amount of hydrogen is absorbed it is given off during solidification of the metal in the ingot mould and results in blow holes and porosity. The hydrogen may be absorbed from the decomposition of moisture under the action of the arc. The moisture may come from damp materials added in the furnace and it has been observed that this condition is most critical in humid weather. Every precaution is taken to dry materials and avoid the introduction of moisture in the furnace. Argon gas for purging hydrogen from the metal bath has proved effective.

Another important method of production in the electric furnace is the so-called single slag practice wherein oxidizing conditions similar to open hearth practice are maintained. A considerable tonnage of rimmed, semi-killed, and fully killed steels is being produced by this method with very good results. These are open hearth grades of steel that do not require superelectric furnace refining; that is, the slag off and refining period is eliminated. Such heats

are produced in less time and at a lower cost than regular electric furnace grades. Faster charging and melting will increase production and reflect a reduction in labor, refractory and maintenance costs, but will not to the same extent reduce power and electrode consumption.

Many of the small and medium sized furnaces are equipped with removable roof mechanism for top charging. This permits much faster charging of the scrap than is possible with the conventional charging machine. This top charge feature has not as yet been engineered into the large 70 ton furnaces but there is much interest in that direction at the present time. Further, a great deal of progress has been made in current regulator controls and larger transformers for increased power input. These improvements should result in increased furnace production, lower costs, and tend to make the electric furnace a closer competitor of the open hearth.

Detroit Section

J. R. Heard, *Secretary-Treasurer*
Wyandotte Chemicals Corporation
Wyandotte, Michigan

The January meeting of the Detroit Section was held on Friday, January 16th, at the Wardell-Sheraton Hotel. The guest speaker for the meeting was Dr. Jesse E. Stareck, Director of Research for United Chromium Corporation, who gave an interesting talk on "Electro-Color and Pattern Plating." The subject of the discussion covered the interesting and novel method of producing the entire range of colors by the controlled electrodeposition of thin films of cuprous oxide and the interesting modifications of the process which lead to the development of electrodeposited patterns.

The Section met again on February 20th at the Wardell-Sheraton. At this time, Dr. John D. Piper, Chemical Supervisor for The Detroit Edison Company, spoke on "Nature of Materials Causing Electrical Conduction Losses in Oils and Impregnated Papers." In his well-organized discussion, Dr. Piper briefly outlined the kinds of electrical equipment employing oils and impregnated papers, the extent to which these insulations may conduct electricity when both new and deteriorated, and means of measurement of the extent of deterioration. This outline was followed by a summary of an extensive investigation designed to show which kinds of deterioration or contamination products significantly affect the power factors and conductivities of these insulations.

Midland Section

Roy C. Kirk, *Secretary-Treasurer*
Dow Chemical Company
Midland, Michigan

The Midland Section met at the Dow Cafeteria on January 8th. The Section members entertained Dr. J. T. Pinkston of the Harshaw Chemical Company in Cleveland at dinner immediately preceding his talk on "The Electrolytic Production of Fluorine." The meeting, open to the public, was well attended. Dr. Pinkston gave an excellent description of the electrolytic process of manufacturing fluorine and of its properties. The equally useful but more easily handled trifluorides of chlorine and bromine were also described. The motion picture "Rubber River" preceded Dr. Pinkston's talk.

The February meeting of the Midland Section was held at the Dow Auditorium on February 3rd and Dr. M. G. Fontana, Professor of Metallurgical Research at Ohio State University, gave an interesting talk on "Corrosion and Corrosion Research." Dr. Fontana's talk was preceded by a paper by H. A. Humble of Dow's Metals Protection Laboratory on "Corrosion of Steel in Sea Water." Also included on the program was the motion picture "Desert Venture."

Dr. Colin G. Fink was the guest of the Section at its March 4th meeting and presented an interesting discussion on several of the topics from his collection of thirty-odd "Unsolved Problems in Electrochemistry" including elimination of pinholes in nickel platinum alloys and disintegration of graphite electrodes in a chlorine cell. The program also included a paper presented by H. K. DeLong of The Dow Chemical Company's Magnesium Laboratories on "Electroplating on Magnesium."

New York Metropolitan Section

J. S. Mackay, *Secretary-Treasurer*
1937 Main Street
Stamford, Connecticut

The guest speaker for the March meeting of the New York Metropolitan Section which was held at the Hotel Holley in New York was Dr. Harry R. Copson who is connected with The International Nickel Company, Inc. in Bayonne, New Jersey. In his talk, "Atmospheric Cor-

rosion of Iron and Steel," Dr. Copson discussed the effect of small alloy additions of copper, nickel, chromium, phosphorus, manganese, and silicon on the atmospheric corrosion behavior of iron and steel. The alloy additions were considered alone and in certain combinations. Dr. Copson stated that under all conditions of exposure alloying seems to be of value, but the magnitude of the benefit and the relative merit of different steels and alloying elements vary. For example, copper and chromium additions seem more effective in industrial atmospheres while manganese seems to be more effective in marine atmospheres.

Some weight loss versus time curves cross. It is unsafe, therefore, to draw general conclusions from tests of limited character. Results were presented showing the effect of location (whether industrial, marine, or rural), of the duration of the tests (the benefit of alloying increases with time), of the manner of exposure (particularly whether sheltered or boldly exposed), of the method of estimating corrosion (whether weight loss, pit depth, or time to disintegration), and of the weather (particularly as regards wetness and pollution). Dr. Copson made frequent reference to theoretical considerations of the problem.

NATIONAL INSTRUMENT CONFERENCE AND EXHIBIT

Philadelphia, Pa., September 13–17 1948

The Third Instrument Conference and Exhibit will be held at Convention Hall, Philadelphia, September 13–17, 1948, sponsored by the Instrument Society of America with the cooperation of the American Institute of Physics, Industrial Instruments and Regulators Committee, American Society of Mechanical Engineers, and Instruments and Measurements Committee, American Institute of Electrical Engineers.

The Press Relations Committee will furnish information on exhibiting companies, technical programs of various cooperating societies, and on the historical exhibit in which will be assembled some of the early American instruments, etc.

Richard Rimbach, *Exhibit Manager*
The Instrument Society of America
1117 Wolfendale St.,
Pittsburgh 12, Pa.

PERSONALS

JOSE M. G. BARREDO, recently with the Bureau of Standards as a guest worker from Spain, is presently associated with the University of Chicago.

G. GERALD DAY is now connected with the Velsicol Corporation, Marshall, Illinois.

JOHN H. GROSS is now a member of the department of Metallurgical Engineering, Lehigh University, Bethlehem, Pa.

C. FRED GURNHAM of Hamden, Conn. has entered the consulting field as a chemical engineer. His principal interests include chemical manufacture, electroplating, and waste disposal.

RALPH HORST has completed his course of instruction at Columbia University and has joined the Research Laboratories of the Aluminum Co. of America at New Kensington, Pa.

GEORGE A. MOORE is now with the Department of Metallurgy at the University of Pennsylvania, Philadelphia, Pa.

MARVIN J. UDY, consulting engineer, has announced the opening of his office in Niagara Falls, New York, for the consulting practice of ferrous and nonferrous process metallurgy and the production of ferro-alloys, phosphorus and calcium carbide, and general electric furnace smelting.

BATTERY SYMPOSIUM IN OCTOBER

The Battery Division is sponsoring a technical session on batteries for the fall meeting of the Society in New York. Dr. G. W. Vinal, Chairman of the Division, will preside. The annual business meeting and election of officers of the Division will also be held at that time. Those wishing to submit papers are urged to send them to the Secretary of the Society before June 15. Other symposia are planned in electrodeposition, electrolytic production of metals, and general and theoretical electrochemistry.

Eleanor Reid, a recent graduate of Cornell University, has succeeded Miss Gladys Garland as a member of the Editorial Staff.

Letters to the Editor

Dear Sir:

I have noted with interest the Journal of The Electrochemical Society and I am much in favor of the publication. However, I want to call one thing to your attention and that is the use of black printing ink on the red cover. It is very difficult to read the type, especially the fine letters on the red background. . . .

M. A. Scheil
Milwaukee, Wisconsin

Dear Sir:

I have just received the first issue of the Journal of The Electrochemical Society and think that it is an excellent idea that a Journal of this type is being published by your society.

Walter A. R. Pertuch
Philadelphia, Pa.

Dear Sir:

I want to congratulate you on the appearance of the first number of the Journal of The Electrochemical Society. It is well gotten up and attractive in appearance. The recent policy of the Society has distinctly raised the average of the contributions.

D. A. MacInnes
New York, N. Y.

Dear Sir:

May I wish you all success in your great task as our new Secretary and for many years to come! I am happy to be able to greet you in this capacity—as I have been faithful to the injunction of Dr. Jos. W. Richards almost 30 years ago: "To remain a member as long as you live."

The information that Dr. Fink retired and you took over as Secretary reached me in the mountains of Norway and I intended to answer you on my return in Brussels in October last, when "unforeseen circumstances" delayed the carrying out of my intentions unduly which I sincerely regret. Yet I hope: better late than never.—What I feel towards your U. S. A., where I got my first job as a chemical engineer, after my degree as such at the Kol. technische Hochschule zu Berlin in Charlottenburg, is aptly expressed in Rudyard Kipling's "The Virginity":

Parsons in pulpits, tax-payers in pews,
Kings on your thrones, you know as well as me,
We've only one virginity to lose,
And where we lost it there our hearts will be!

To this I may add the remembrance of faithful friends and great kindness that I met and never forget "over there" in our Society and outside it—in Perth Amboy, New York, Niagara Falls and Philadelphia and its suburbs. I am glad to live long enough to have got an occasion to express my thankfulness to so many friends and for the opportunity your great nation gave me, and so many others from this side, to get work at a time when openings were scarce in Europe. I can never forget, nor the splendid N.W. trip of 1927 and new-found friends.

And now the time has come that my eldest son, Georges, is planning a visit to U. S. as a change from his diplomatic service at the Belgian Legation at Oslo (my two other sons are secretaries of the Norwegian Embassies at Paris and Stockholm: Axel and Olow—Axel recently returned to the F.O. at Oslo).

Will you and members of our Society receive Georges kindly when soon, or later, he may call on you and ask for information with a view of perhaps returning to stay in U. S.? Once you have seen him you will readily recognize him anywhere, with his 6'6" he is not easily overlooked. Besides 13 years at the Belgian Legation in Oslo (interrupted by a short imprisonment by the Germans or Quislings and a year's work at the British Legation at Stockholm after he fled from Norway, finally to serve in Scotland and Norway as a liaison-officer to the Allied Forces), he had spent a year in Morocco as Assistant Superintendent to a great wine-yard acquiring a fairly good knowledge of Arab, added to his thorough knowledge of French, Norwegian and English (Swedish and Danish) and rudiments of Dutch and German, and mechanical skill (he has

constructed an army light carrier-car and stretcher which is on the point of being adopted on this side)—well, you may see for yourself when he arrives in N. Y. to have a look round. The peaceful, roving viking spirit. Of course, like any young man from German-occupied Europe and resistings to the enemy, Georges and his brothers have their wartime tales to tell—how one of them pressed himself out through the bars 7″ apart of his prison window 40′ above ground and escaped—I am told the Washington or Saturday Evening Post have referred to his adventures. He does not want to speak of it himself—a history like millions others all over the world.

May I add my sincere gratitude to you and any one, who may kindly and helpfully guide him in his pilgrimage.

Norway has been in want of hydro-electric power. The spring, summer and fall of 1947 will long be remembered in Norway in the S.E. part especially. There are no records of any year of such prolonged drought, a Mediterranean summer settled over S.E. Norway with dry winds, sunny days (most delightful for tourists) and no rain whatever for weeks and months on end. Highland marshes dried up, brooks were empty, wells held no water, river basins and storage lakes were at low level, glaciers melted away, fields and crops dried up, trees died for lack of rain. A stone appeared in a lake in S. E. Norway marked A.D. 1721. History tells there was a drought in Europe about that time. (A similar occurrence from last summer records a like stone to have appeared in the Danube with an inscription predicting famine when it was found again.)

As a consequence I took across the marshes last summer when up in the Highland instead of walking round them, they were dry. Cattle had to be killed off for lack of hay and fodder. Electric street lamps are shut off during the nights this winter in Oslo and Eastern towns and for some hours during daytime too, also for house-heating. The lack of hydro-electric power is a bottleneck on industries in the center and East Norway. It will take four to five years to furnish from new power stations sufficient power to insure against another such year. The war slowed down the development of the rich water resources of Norway, lack of machinery delayed deliveries and lack of dollars are other bottlenecks in the harnessing of new water-powers. Norway too expects a helping hand from Mr. Marshall's plan and needs it.

Ivar J. Moltkehansen
Brussels, Belgium

Dear Sir:

Frankly I am disappointed. I had hoped for a scholarly publication like the Transactions of the Faraday Society or other American journals like the Journal of the American Chemical Society; instead I open it up to find eight pages of news items. Why cannot such matters be published on a separate sheet sent out with the Journal if necessary? Also I don't like the size and shape or the way in which the contents are printed inside of the front cover instead of outside. However the latter objections are purely personal. Another thing, who is the editor of the Journal? I see Burns's name as editor of editorial staff and then I read an editorial signed J. A. L. who is presumably chairman of the Editorial Board. I see O. W. Storey as Chairman of the Publication Committee. I would suggest that a real editor be appointed and a Board of Associate Editors established who are competent to review papers in their special fields. Let them do most of the critical reviewing.

Anon.

● While it will not be the policy of the Journal to print unsigned communications, the above criticism is of sufficient interest to publish and offer explanatory comments. The Editor would be grateful for sufficient volume of high quality technical manuscripts to make the Journal, especially in its early issues, comparable to the examples cited. Perhaps our correspondent will supply some acceptable papers.

With respect to news items, it is believed that the majority of members and readers desire to be informed on matters of current interest. The practice adopted by the Journal follows that of the publications of several other societies. The American Chemical Society with its twenty two-fold larger membership is able to publish a separate news journal. Concerning editorials, it may be said that the Editor does not expect to contribute all of the editorials which will appear in the Journal.

The Publication Committee is composed of men particularly competent to review papers in all of the special fields covered by the Society and has sole

responsibility for the acceptance of all technical papers.

The Editorial Board acts as an advisory body to the Editor on matters of editorial and publication policy.

Finally as to the size of the Journal, this was determined by the decision to continue the Transactions in their present format, for the technical papers for both the Journal and Transactions are printed at the same time thereby realizing very sizeable and necessary economies—Ed.

YOUNG AUTHORS AND TURNER BOOK PRIZES AWARDED

Mr. Henry Leidheiser, Jr., Research Assistant at the University of Virginia, has been named the recipient of the Young Authors Prize for 1948. His contribution, "The Influence of Crystal Face on the Electrochemical Properties of a Single Crystal of Copper" (preprint 91-6), was judged the best of all eligible papers presented before the Society at the Louisville and Boston meetings.

Mr. Austin E. Hardy, of the Radio Corporation of America, Lancaster, Pa., was selected by the judges to receive the 1948 Turner Book Prize for his paper, "A Combination Phosphorometer and Spectroradiometer for Luminescent Materials" (preprint 91-8). Mr. Hardy, it will be recalled, was the winner of the Young Authors Prize in 1946.

COURSE IN ELECTROCHEMISTRY

A seminar course in Electrochemical Operations is offered at the University of California this spring under the auspices of the Chemical Engineering Division. The course will stress principles and empirical methods especially usable in the design of new electrochemical processes. Close attention will be given to such subjects as concentration, polarization, kinetics of electrode processes, hydrogen-oxygen overvoltage, theory of potential, thermodynamics of fused salts, principles of deposition and dissolution, material and constructional problems. Students will do some research in the literature and give reports on selected subjects; discussions will be based on recent papers of The Electrochemical Society and the Zeitschrift für Elektrochemie.

Dr. Charles W. Tobias will direct the seminar with the cooperation of Professors Latimer, Orlemann, and Vermeulen.

POSITIONS AVAILABLE

ELECTROCHEMICAL ENGINEER, thoroughly familiar with the manufacture and production of dry cell flashlight batteries to take charge of new battery manufacturing plant in Colombia, South America. Reply to Box A-199, The Electrochemical Society, Inc., 235 West 102nd St., New York 25, N. Y.

CORROSION ENGINEER, extensive industrial experience in physical metallurgy, corrosion, and materials of construction in the chemical industry required. Location southwest. Reply to Box A-200, The Electrochemical Society, Inc., 235 West 102nd St., New York 25, N. Y.

ELECTROCHEMIST, qualified, responsible, for permanent position with established Eastern Dry Battery manufacturer. Development and manufacturing experience in dry batteries preferred. Salary commensurate with responsibility. All replies to be held confidential. Reply to Box A-201, The Electrochemical Society, Inc., 235 West 102nd St., New York 25, N. Y.

POSITIONS WANTED

ELECTROCHEMIST, broad experience in research, development process control, industrial materials, engineering, and finishing methods. Metropolitan New York or New England area preferred. Reply to Box 317, The Electrochemical Society, Inc., 235 West 102nd St., New York 25, N. Y.

CHEMICAL ENGINEER, age 27, experienced in organic and inorganic metal finishing. Seeks position in sales or research department of progressive firm. Reply to Box 318, The Electrochemical Society, Inc., 235 West 102nd St., New York 25, N. Y.

METALLURGIST, B.S. (Chem.), age 36, post-graduate work in metallurgy, desires position in production and refining of non-ferrous metals. Experienced in process development applying furnace, electrolytic, and leaching methods to production and refining of copper, lead, silver, tin, cadmium, zinc, and other metals. Location secondary. Reply to Box 319, The Electrochemical Society, Inc., 235 West 102nd St., New York 25, N. Y.

NEW MEMBERS

At the meeting of the Board of Directors held on March 5, 1948 at the Bell Telephone Laboratories, Murray Hill, New Jersey, the following were elected to membership:

DONALD H. BISSELL, Chromium Corp. of America, mailing add: Room 2212, 120 Broadway, N. Y. 5, N. Y. (Electrodeposition)

ELLSWORTH T. CANDEE, The Lea Mfg. Co., 16 Cherry Ave., Waterbury 86, Conn. (Electrodeposition)

ALBERT D. EPLETT, Manning, Maxwell and Moore, Inc., 11 Elias St., Bridgeport, Conn. (Corrosion, Electrodeposition, Electronics)

J. BYRON GODSHALL, Ingersoll-Rand Co., Phillipsburg, N. J. (Corrosion)

RAYMOND C. HAEFNER, Autolite Battery Corporation, Niagara Falls, N. Y. (Batteries)

JOHN F. KASZYNSKI, Witco Chemical Co., 6201 W. 51st St., Chicago 38, Ill. (Corrosion)

WILLIAM ALLEN MAXWELL, Climax Molybdenum Co. of Pa., mailing add: 14 Dinsmore Ave., Burgettstown, Pa. (Theoretical Electrochem., Electrodeposition, Electrothermics)

JOSEPH EMMOR MILLARD, Dow Chemical Co., Freeport, Texas. (Alkali and Chlorine)

DOUGLAS E. PATON, Sydenham Trading Co., mailing add: 8 McNaughton Ave., Wallaceburg, Ont., Canada. (Organic Electrochem., Electrodeposition)

SIGMUND SCHULDINER, Naval Research Lab., mailing add: 2112—32nd Pl. S.E. Washington 20, D. C. (Corrosion)

J. WILLIAM WIGERT, Westinghouse Electric Corp. 1216 W. 58th St., Cleveland, Ohio. (Theoretical Electrochem., Corrosion, Electrodeposition, Electrothermics, Dielectrics)

ROBERT A. WILLIHNGANZ, Linde Air Products Co., mailing add: 284 Washington Ave., Kenmore 17, N. Y. (Corrosion)

REINSTATEMENT

LELAND M. MORSE, 3289 Interlaken, R.D. 3, Pontiac, Michigan.

ERRATUM

March Journal, p. 76, Fig. 12. 1.3 A should read 2.1 A and 1.5 A should read 1.8+ A.

PATENTS OF INTEREST TO ELECTROCHEMISTS

Selected by Fred W. Dodson, Chairman of the Patent Committee, from the Official Gazette

January 27, 1948

Johnson, J. B., 2,434,930, Method and Apparatus for Ionic Discharge Coating

Johnson, J. B., 2,434,931 Method and Apparatus for Ionic Discharge Coating

Richards, E. A., 2,434,960, Metal Rectifier

Skinker, M. F., Denyssen, I. P., and Kolmes, M. G., 2,434,967, Rectifier and Method of Making the Same

February 3, 1948

Adler, O. E., 2,435,191, Rubber Coated Steel Object

Christensen, N. C., 2,435,340, Process for the Treatment of Marmatitic Zinc Ores

Keller, H., and Ehrensperger, C., 2,435,357, Device for Igniting and Energizing Mercury Arc Rectifiers

Werner, C. A., 2,435,375, Battery Bracket and Holder

Pettingill, R. J., 2,435,463, Adjustable Battery Carriage

Williams, J. S., and Binai, W. R., 2,435,525, Electrodeposition of Silver from a High Silver Cyanide Content Bath

RECENT PUBLICATIONS OF THE NATIONAL BUREAU OF STANDARDS

The following publications of the National Bureau of Standards became available during January. Copies may be obtained from the Superintendent of Documents, Government Printing Office, Washington 25, D. C.

Electrodeposition of Tungsten Alloys Containing Iron, Nickel, and Cobalt, Abner Brenner, Polly Burkhead, and Emma Seegmiller, 33 pp. RP1834.

Deposition of Nickel and Cobalt by Chemical Reduction, Abner Brenner and Grace Riddell, 11 pp. RP1835.

Calculations on Countercurrent Electromigration, G. Breit and F. L. Friedman, 13 pp. RP1836.

Activity Coefficients in Aqueous Mixtures of Phosphates with Sodium Chloride, Sodium Bromide, and Sodium Iodide, and the pH of Phosphate Buffer Solutions, Roger G. Bates, 7 pp. RP1837.

Two Signs of the Times

The sign in front of a number makes a whale of a difference. The skeptic need only let his bank balance shift to a negative sign and he will be reminded of his error rapidly and officially. Then again, the annual balance of a well-managed business practically always comes out with a positive sign. In science and technology, however, we have both positive and negative values of temperature, electrochemical potential, and Rh factor. The sign makes the differences between freezing and thawing, it can distinguish between passivity and activity, and finally, sometimes life or death.

With electrochemistry, the correct sign of an electrode potential, despite its importance, is not generally agreed to. There exist two camps of thought on the matter, divided into large groups of scientists and engineers the world over. The situation is bewildering, especially to students who begin courses in electrochemistry, and there is waste of human effort each time an author explains which system he is using, if not more often from misunderstanding caused by *lack* of such explanation.

The circumstances that led to confusion in the first place seem to have begun about 1913 with a paper published by G. N. Lewis reversing the usage adopted in 1911 by Abegg, Auerbach, and Luther. Five years later a committee appointed by the Electrochemical Society reported preference for the convention used by the Bunsen Gesellschaft (Abegg, Auerbach, and Luther) and the Faraday Society. G. N. Lewis in his publications, however, persisted in the use of the opposite sign on the basis that his survey of previous literature favored his choice; this is demonstrated in "Thermodynamics" which he published with Randall in 1923. The book became standard among chemists in America resulting generally in adoption of the Lewis system. With time, the confusion grew worse rather than better.

When the "Corrosion Handbook" was organized and the question of sign again came up, the Editor wrote the late Professor G. N. Lewis asking him whether any justification existed for one sign over the other. Professor Lewis replied, "It is a good deal like choosing between the right hand and the left hand drive for an automobile. We thought when we published our book that our choice of sign was the one that conformed to the best of the previous literature, and since then, of course, nearly all chemists have adopted our conventions. If you change that sign now, you will never get the thousands of chemists who use Lewis and Randall to agree with you."

Some chemists concur with Professor Lewis in the feeling that it is impossible now to change the situation. Official international action can force no one to abide, but it certainly can, like the dictionary, point to the preferred sign.

H. H. U.

News Notes

NATIONAL OFFICERS ELECTED

Mr. Lee

Mr. Hunter

At the Annual Business Meeting held in Columbus during the 93rd Convention, the committee of tellers reported the results of the recent balloting and announced the election of James A. Lee to the office of President of The Electrochemical Society. Ralph M. Hunter has been elected the new Vice President, and William W. Winship and R. M. Burns have been returned to their respective offices of Treasurer and Secretary.

Mr. Lee, managing editor of "Chemical Engineering" magazine, succeeds George W. Heise who becomes Past President of the Society, the post automatically filled by the retiring President. Accession to the presidency culminates Mr. Lee's long period of service on the Board of Directors.

Mr. Hunter now joins Vice Presidents A. L. Ferguson and C. L. Faust on the Board. An active member of the Midland Section, Mr. Hunter is manager of the Electrochemical Division of the Dow Chemical Company.

A special session of the Board of Directors was held on Friday, April 16th, at the request of the new President. Existing vacancies on several of the Society's committees were filled by appointment of the President and approval of the Board. The Executive Committee now consists of James A. Lee, R. M. Burns, W. W. Winship, and E. G. Widell.

R. M. Hunter was appointed Chairman of the Ways and Means Committee and O. W. Storey was again approved for the post of Chairman of the Publication Committee. L. I. Gilbertson will serve for the coming year as Chairman of the Editorial Board and R. S. Mackie will direct the activities of the Membership Committee.

THE USE OF PLASTIC BEADS ON CHROME PLATING TANKS

ARTHUR C. STERN, LAWRENCE P. BENJAMIN, AND HARRY GOLDBERG

Division of Industrial Hygiene and Safety Standards New York State Department of Labor

[*Condensed Version*]

In the process of electroplating, a mist is generated by bubbles of hydrogen and oxygen rising from the electrodes. These bubbles burst on the liquid surface and disperse minute droplets of the plating solution into the air.

In chromium plating, these droplets consist of a concentrated solution of chromic acid and, as such, constitute the hazard arising out of this operation. This hazard frequently manifests itself in the form of a severe dermatitis and skin ulcerations if prolonged contact is allowed or a perforated septum under conditions of prolonged exposure to inhalation. In order to minimize this dispersion of chromic acid, it is necessary to provide some means for the control of the mist. It has been found from experience that local exhaust ventilation, applied laterally from two sides, using slots from one to two inches wide depending on the width of the tank and using a ventilation rate of 120 to 150 CFM per sq. ft. of tank area provides adequate control. The maximum allowable concentration of chromic acid mist in the atmosphere is generally accepted as 0.1 mg. per cubic meter.

The tests herein reported were undertaken after a number of chrome plating establishments requested permission to use a plastic layer (either rods or tubes) as a substitute for, or an adjunct to, conventional ventilation. The study was conducted during the winter of 1946–1947 and covers studies in six different plating establishments in New York City.

BEAD DESCRIPTION AND FUNCTION

The rods or tubes (collectively called beads) used in these tests were fabricated from plastic polystyrene. The rods were solid lengths, $1\frac{1}{4}''$ long and $\frac{1}{8}''$ diameter. The tubes were hollow lengths of $\frac{1}{4}''$ diameter tubing, $2\frac{3}{4}''$ long, pinched and sealed at the ends. The specific gravity of the rods and beads is such that they float on chromic acid. The rods sink in water but the tubes, because they are hollow, float on water as well. Which of these characteristics is preferable depends on individual preference.

The primary function of the beads floating on the liquid surface is to provide a large solid surface area against which the ascending bubbles can break and thus allow the gases to escape at the surface of the liquid without bursting violently. The secondary function is to provide a large wetted surface against which the mist droplets formed by the bursting bubbles can impinge and thereby be trapped. The bead layer in immediate contact with the liquid surface provides the solid surface area against which the bubbles burst. Any successive layers of beads perform the function of trapping the chromic acid droplets by impingement.

A loading of one pound of solid rods per sq. ft. of tank surface yields a blanket about $\frac{1}{4}''$ thick. A loading of one pound of tubes per sq. ft. yields a $\frac{3}{4}''$ blanket of beads. The rods appear to cover the tank surface more completely because of their smaller dimensions.

Light wired work was found not rigid enough to spread a heavy bead layer apart. It was seen that the operator had to expose a portion of liquid area before introducing the work and, after it was lowered, had to push the beads back into position again. If the beads were not pushed back it became evident that liquid currents caused by the rising bubbles separated the beads and prevented them from providing an effective cover. Where the work to be plated was structurally rigid and massive or was rigidly supported on a rack, the work itself, when introduced, spread the beads apart sufficient for entry and allowed them to return to position before the updraft of bubbles started.

PROCEDURES

Physical data were obtained on the six tanks, each of which was in a different plant along with the measured ventilation rate at the tank. The tanks were typical of normal plating room design and the ventilation rate reasonably close to what is considered good practice. Rods were used in two plants and tubes in four plants. The test procedure in general was first to measure chromic acid concentration in the general breathing zone of the operator, without any beads in the tank, with the ventilation system turned on, and again with it turned off. Then, an initial thin layer of the beads under test were placed on the tank and measurements again made of chromic acid mist concentration with ventilation on and off. Further layers of beads were added and the same procedure repeated until the thickest layer to be tested was in the tank.

All air samples were obtained using the Hatch modification of the Greenburg-Smith Impinger filled with 75 cc of 0.01N sodium hydroxide absorbing solution. The rate of sampling varied between a low of 0.85 CFM and a high of 0.95 CFM, the average being at about 0.90 CFM. Sampling at tests with exhaust ventilation were continued until a yellow tinge could be seen in the absorbing solution. Sampling at tests with exhaust ventilation were continued for either approximately one hour, or were stopped if the yellow tinge appeared in the absorbing solution in a shorter time. In two plants chromic acid was analyzed iodometrically using 0.01N sodium thiosulfate ($Na_2S_2O_3$). It was found that the lower limit of sensitivity of this method was approximately 0.05 mg. of chromic acid per cubic meter of air. Since most of the tests with ventilation yielded results below the lower limit of sensitivity of the method, a more sensitive method was adopted for the four remaining tests. For these tests, chromic acid was analyzed colorimetrically with *diphenylcarbazide*. The lower limit of sensitivity of this method of analysis is approximately 0.001 mg. of chromic acid per cubic meter of air and, even in this case, a large proportion of the results on tanks with ventilation were below the lower limit of sensitivity of the analysis. It is, therefore, highly probable that the three test results in the first two plants which were below the lower limit of sensitivity of the method of analysis originally employed are actually nearer or less than 0.001 mg. per cubic meter rather than less than 0.05 mg. per cubic meter as is reported herein.

In all of the plants where tests were made, room ventilation was a variable factor. In the particular case of plant #3, note was made of strong room drafts away from the breathing zone of the operator. Room drafts of lesser magnitude, of course, influenced to some extent all of the other test results. It was found that there is a very definite lowering of chromic acid concentrations with increased thicknesses of bead layer. The most marked decrease occurred with a relatively thin bead layer. Very little further decrease was obtainable with thicknesses beyond one inch. It was also found that a tenfold reduction in chromic acid concentration was obtainable by a bead layer of the order of from $\frac{3}{4}$" to $1\frac{1}{4}$" thick. However, employing a bead layer alone, the concentration at the breathing zone was not lowered to the maximum allowable concentration of 0.1 mg. per cubic meter. Hence beads may not be used as a substitute for exhaust ventilation. The lowest concentration which can be obtained in the breathing zone of the workman is from four to six times maximum allowable concentration according to the manufacturers of these beads.

CONCLUSIONS

It does not seem wise to recommend any decrease in the required ventilation rate for chrome plating tanks because of the addition of plastic beads. The principal reasons for this recommendation are (1) resistance of operators to the use of beads; (2) the possibility of "drag-out" losses reducing the bead layer to a point below which it ceases to afford maximum effectiveness; (3) the possibility of failure to initially provide a quantity of beads sufficient for maximum effectiveness; and (4) the possibility of operating the tank with the beads pushed back to the tank walls leaving the central liquid area uncovered.

In general, it may be concluded that plastic beads are effective in decreasing the rate of chromic acid mist dissemination from the surface of chrome plating tanks.

The assistance of Hanson, Van Winkle & Munning, Lea Manufacturing Company, and The Udylite Corporation for supplying the beads used for this series of tests and for their generous cooperation and technical assistance is acknowledged.

SECTION NEWS

Cleveland Section

C. B. Sanborn, *Secretary-Treasurer*

2231 Wrenford Road
University Heights 18, Ohio

The March meeting of the Cleveland Section was held at the Hotel Carter in Cleveland on March 9th. The guest speaker at this time, Dr. Sherlock Swann, Jr., Research Professor of Chemical Engineering at the University of Illinois, spoke on "Electrolytic Reduction of Carbonyl Compounds." In his talk, Dr. Swann discussed the electrolytic reduction of ketones, aldehydes, acids, and amines and then showed the influence of the cathode material and the nature of the catholyte. It was pointed out that in acid solution the metals in the second group of the periodic table together with lead are, in general, the most active cathodes. Further, Dr. Swann stressed the importance of the physical structure of the cathode material. Illustrations were given of the effects of cold work, etching, and alloy formation; studies of reductions at different types of carbon cathodes were also reported. Many more cathodes were found to be active in alkaline solution than in acid solution. Two examples of reductions in glacial acetic were shown.

Detroit Section

J. R. Heard, Jr., *Secretary-Treasurer*

Wyandotte Chemicals Corporation
Wyandotte, Michigan

The Detroit Section met on Friday, March 19th at 8:00 P. M. at the Wardell Sheraton Hotel, Woodward at Kirby, Detroit. The guest speaker for the meeting was Dr. Henry Brown of The Udylite Corporation in Detroit. The subject of the talk was "Porosity of Electrodeposits" and Dr. Brown, who has had considerable experience in the electroplating field, discussed inherent and induced porosity of electrodeposits and inclusions in electrodeposits. In addition, a summary was given of some salt spray studies on brass coatings on steel, nickel coatings on steel, and nickel foils.

Pittsburgh Section

R. Rimbach, *Secretary*

1117 Wolfendale Street
Pittsburgh 12, Pennsylvania

A joint meeting of the Pittsburgh Section of the Electrochemical Society and the Corrosion Forum was held on Monday, March 8th at the Hotel Henry in Pittsburgh. Before the meeting, members and guests enjoyed dinner in the Charles Dickens Room of the hotel.

The guest speaker for the occasion, Mr. Sidney Barnartt of Westinghouse Research Laboratories, discussed a new subject that has provoked a great deal of interest in the electroplating industry, "Electroplating with Periodic Reverse Currents." In his talk, Mr. Barnartt presented the fundamental considerations involved in electroplating with Periodic Reverse currents. In addition, the benefits that have been secured by substituting Periodic Reverse currents for D.C. were illustrated by means of photomicrographs of copper plating from the simple acid bath and from the complex cyanide bath. These benefits include better metal distribution, smoother and brighter deposits, reduced porosity, increased plating rate, and heavier deposits of smooth, sound metal.

Also included on the program, through the courtesy of the American Hot Dip Galvanizers' Association, was the motion picture, "Must It Rust" which showed the steel base metal actually rusting as viewed through a microscope. The "cleaning" of the base metal by the pickling process was shown and explained as was "galvanizing" of various products, metallurgical photographs of the construction of a zinc coating by Hot Dip Galvanizing, and an explanation of its formation.

BATTERY ORGANIZATIONS BECOME SUSTAINING MEMBERS

New additions to the Sustaining Membership of the Society are the Willard Storage Battery Company of Cleveland, Ohio and the Electric Storage Battery Company of Philadelphia, Pennsylvania. The generous support provided by these organizations is appreciated and will be of substantial aid in the development of the Battery Division in its fields of activity.

C. F. BONILLA TO JOIN FACULTY AT COLUMBIA

Dean James K. Finch has just announced the appointment of Dr. Charles F. Bonilla as Professor of Chemical Engineering at Columbia University. As a member of the faculty at Columbia, Dr. Bonilla, a former student of Dr. Colin G. Fink, will direct research and teach in the field of chemical engineering thermodynamics.

Dr. Bonilla graduated from Cuenca Institute in Spain and holds undergraduate degrees in electrical and chemical engineering and a doctorate in electrochemistry from Columbia. Before occupying his present position as Professor of Chemical Engineering at

DR. BONILLA

Johns Hopkins University in Baltimore, Md., he taught at several colleges and universities. Further, Dr. Bonilla has, as a consultant, been associated with the Chesapeake Chemical Company, the Main Salvage Equipment Company, the Phillips Petroleum Company, and the U. S. Board of Economic Warfare; he has also been a member of a number of economic missions sent by the U. S. government to Brazil and Cuba.

A leading specialist in high pressure reactions in the field of chemical engineering, Dr. Bonilla has been an active participant in the affairs of the Society since he joined in 1931 having prepared the Spanish abstracts for the technical articles published as preprints and appearing in the Transactions.

PERSONALS

BASIL G. APOSTLE, in his new position as Research Chemist with the National Aniline Division of the Allied Chemical & Dye Corporation in Buffalo, N. Y., is engaged in research and development on catalysts.

LORAN A. CREGLOW has recently become affiliated with the U. S. Smelting Refining and Mining Company in Midvale, Utah. Mr. Creglow was formerly with the Research Laboratory of that establishment in Cambridge, Mass.

PAUL F. HOGLUND, former Resident Chemist for the Electroplating Section of E. I. du Pont de Nemours & Co., Inc. in Cleveland, Ohio is now with that firm's Grasselli Chemicals Department in Grasselli, N. J.

HELEN D. HOOVER, formerly with the Alhberg Bearing Company in Chicago, has taken a position in the Physics Laboratory of International Harvester Manufacturing Research in that city.

WILBUR A. LAZIER, Director of the Southern Research Institute for the past three and one-half years, became Director of Chemical Research for Chas. Pfizer & Co., Inc. on April 11, 1948.

The Society regrets to announce the death of one of its charter members, Dr. G. B. Frankforter. Dr. Frankforter, born on April 22, 1859 in Potter, Ohio, received his A.B. degree from the University of Nebraska in 1886 and his doctorate in Berlin in 1893. He became Professor of Chemistry at the University of Nebraska and, from 1894 to 1917, was Dean and Director of the School of Chemistry at Minnesota. During World War I, he was a member of the Ordinance Claim Board and technical advisor to the States Committee. Later, he returned to Minnesota as Professor of Organic and Industrial Organic Chemistry; he subsequently became a member of the faculty at Stanford University.

Dr. Frankforter was the 78th member of the Society, having joined on April 3, 1902; he had been an emeritus member for the past ten years.

Letters to the Editor

Dear Sir:

I recently received a copy of the Corrosion Handbook. It certainly is a very impressive volume. The Society and Herb Uhlig deserve a great deal of credit for seeing this project to completion. I would predict that the Handbook will have a very successful career.

I also wish to comment very favorably upon the new Journal of The Electrochemical Society. All of these matters indicate that the Society is definitely on the upgrade, and will play a much more important role in the future than it has in the past.

J. C. Warner
Pittsburgh, Pa.

Dear Sir:

In connection with voting by mail ballot, I wondered if you might see fit to accompany the voting slips with a short biographical sketch of each of the candidates. The Chemical Institute of Canada has adopted this policy as it had been suggested that a good deal more interest might be stimulated among the voting members if this were done. . . .

E. P. Blandy
Port Credit, Ontario

Dear Sir:

I was interested in the response to the membership questionnaire published in the Journal. More responses were received from the Electrodeposition Division than from any other Division.

This was of special interest to me as I was the first Chairman of the Electroplating Committee which later became the Electrodeposition Division of which I had also the honor of being the first Chairman.

As Chairman of the Membership Committee it was my good fortune to interest a number of electroplaters in The Electrochemical Society and by personal contact was able to increase the membership of the Society 18 per cent that year.

The Electrodeposition Division has proved faithful!

George B. Hogaboom
New Britain, Conn.

Dear Sir:

There appears to be some confusion about the relationship of papers published in the Journal and those which appear in the Transactions of the Society; I should appreciate an explanation of the matter in the Journal for the benefit of the membership.

All material which appears in the Technical Section of the Journal will also appear in the Transactions. The pagination is continuous in the technical sections of successive Journals and will be duplicated in the Transactions. When the Journal is printed, enough extra copies of the Technical Section are run off to meet the estimated demand for copies of the Transactions; a separate printing is not made for the Transactions and, for this reason, the discussion of any paper will be found in a separate section of the bound volume.

A divisional representative of the Publication Committee may recommend a technical article for publication in the News Section of the Journal in which case the article would not appear in the Transactions. This judgment is applied to those articles which, it is felt, are of passing interest only.

O. W. Storey
Chicago, Illinois

Dear Sir:

Your editorial in the March number was apropos and points to a situation that we in the universities should do something about. As yet, however, I am not certain of the method whereby we can screen out men who show lack of orginality. Usually, the hope is that a man with good grades will develop during his first or second year of graduate studies. Perhaps one solution is to stop a man with a master's degree should our predictions about his ability go astray. . . .

H. H. Uhlig
Cambridge, Mass.

Dear Sir:

I like very much the Journal of The Electrochemical Society and feel confident it will serve a most useful purpose.

W. A. Hamor
Pittsburgh, Pa.

INTERNATIONAL CONFERENCE ON SURFACE REACTIONS

An attractive program has been arranged for the Pittsburgh International Conference on Surface Reactions to be held at the Mellon Institute, June 7–11, 1948.

The first session will be devoted to addresses of a general nature by D. R. Weidlein of the Mellon Institute, R. E. Zimmerman of the U. S. Steel Corp., R. M. Burns of Bell Telephone Labs., and W. H. J. Vernon of the Chemical Research Labs. in Teddington, England.

More than thirty papers will be presented before the nine technical sessions by authorities in the field of surface reactions. Among those who will present papers are the following: Cecil King, Martin Kilpatrick, Walter Kauzman, Paul Thorhodin, Carl Wagner, G. Valensi, M. Fontana, W. C. Leslie, A. T. Gwathmey, Charles L. Faust, A. B. Winterbottom, N. A. Nielsen, E. M. Mahla, T. W. Sellwood, T. H. Emmett, J. W. Hickman, E. A. Gulbransen, M. A. Streicher, G. Benedicks, Fred Keller, J. B. Edwards, R. W. Gurney, K. Andrews, G. Chaudron, M. Bernard and W. E. Campbell.

In addition to the technical sessions, there will be opportunities for visiting various research laboratories in the Pittsburgh area. The conference is sponsored by the Pittsburgh Section of The Electrochemical Society. Dr. E. A. Gulbransen is Chairman of the Conference and the Secretary is Richard Rimbach, 1117 Wolfendale Street, Pittsburgh, Pa.

A.A.A.S. CORROSION CONFERENCE

The annual corrosion conference sponsored by the American Association for the Advancement of Science will be held at Colby Junior College, New London, New Hampshire, July 26 to 30 inclusive. Dr. I. A. Denison of the National Bureau of Standards will be Chairman and Dr. H. R. Copson of the International Nickel Company, Vice-Chairman of the Conference. The program will be as follows:

"Oxide Films" by R. B. Mears, Carnegie-Illinois Steel Corp., and Marshall Brown of E. I. du Pont de Nemours & Co.

"Absorbed Films" by M. G. Fontana, Ohio State University, and Norman Hackerman of University of Texas.

"Electron Configuration and Related Phenomena of Metal Dissolution" by H. H. Uhlig of Massachusetts Institute of Technology.

"Surface Reactions Occurring in Vacuo and in Low Pressure Gas Atmospheres at High Temperatures" by E. A. Gulbransen, Westinghouse Electric Corporation.

"Surface Free Energy and Its Possible Role in Corrosion Processes" by Adam S. Skapski, Institute for the Study of Metals, University of Chicago.

"Depolarizers and the Diffusion Layer of Metal Dissolution" by C. V. King, New York University.

"Chemical Activity of Metal Surfaces to Oxygen" by T. N. Rhodin, Jr., Institute for the Study of Metals, University of Chicago.

"Generalized Theory of Corrosion Inhibition" by Norman Hackerman, University of Texas.

"Measurement of Polarization by the Pulse Polarizer" by H. J. McDonald, Illinois Institute of Technology.

"Microscopic and Diffraction Methods Applied to Corrosion Problems" by Keith H. Storks, Bell Telephone Laboratories.

"Correlation of Metallographic Techniques in Magnesium Corrosion Studies" by W. S. Loose, Dow Chemical Company.

"Application of the Polarograph to Corrosion Studies" by Pierre Van Rysselberghe, University of Oregon.

"Measurement of Surface Roughness of Metals" by Thomas P. May, International Nickel Company.

"Weather Factors in Atmospheric Corrosion Tests" by O. B. Ellis, American Rolling Mill Company.

Applications for attendance at the Conference should be sent to Dr. W. George Parks, Department of Chemistry, Rhode Island State College, Kingston, R. I.

A.I.E.E. MEETS IN NEW HAVEN

The North Eastern District Meeting of the American Institute of Electrical Engineers was held on April 28th, 29th, and 30th in New Haven, Conn; meeting headquarters were in the Hotel Taft. Programs for the various sessions consisted of technical papers covering numerous subjects of interest to electrical engineers. Included were papers published by the Institute and a group of district papers intended for presentation only.

The program for Wednesday morning, the 28th, consisted of simultaneous sessions on Rotating Machinery; Transformers, Cables, and Insulation; and Instruments and Electronics. Wednesday afternoon included sessions on Industry Applications—Textile Machinery, Circuit Breakers and Switchgear, and Special Industry Applications. Thursday's sessions included papers presented on the general subjects of Power and Land Transportation, Relays and Protective Devices, and Wire Drawing Machinery; Friday's program included discussions of Special Industrial Applications and Heating, Communication, and a special session devoted to papers presented by students from neighboring institutions.

The principal addresses for the meeting were delivered on Thursday morning during the General Session by T. J. Russell, Chairman of the Connecticut Technical Council and C. W. Mayott, Connecticut Valley Power Exchange. Mr. Russell spoke on "Conservation of our Nation's Natural Resources" and Mr. Mayott discussed "Electric Power Supply of the United States with Special Emphasis on the Northeast."

An interesting program was planned for the ladies and inspection trips were made to various industrial plants around New Haven including such places as General Electric Company in Bridgeport where the wire and cable division showed the manufacturing and insulating of building wire, BX Cable and power cables; Winchester Repeating Arms Co. with an inspection of its manufacturing processes; Dunham Laboratory of Yale University with a demonstration of ultra-high frequency equipment, electronic applications, communication equipment, and servo-mechanisms.

ATOMIC ENERGY COMMISSION FELLOWSHIPS

The National Research Council is announcing a new program of fellowships supported by funds provided by the Atomic Energy Commission as a part of the Commission's responsibility for future atomic energy research. Accordingly, these fellowships will be awarded in the many fields of science related to research in atomic energy and the products of atomic energy processes. A considerable number of these fellowships are available to young men and women who wish to continue in graduate training or research for the doctorate in an appropriate field of science, others will provide training in biophysics applied to the control of radiation hazards, and an additional number of fellowships will be assigned to those below the age of 35 who have already achieved the doctorate and who wish to secure advanced research training and experience in those aspects of the physical, biological and medical sciences related to atomic energy.

The candidates will be selected by fellowship boards of the National Research Council established for this program. In the postdoctoral field, there will be three groups of fellowships. For the selection of fellows for advanced research and training in the general field of the physical sciences, a board has been established with Dr. Roger Adams, Professor of Chemistry, University of Illinois, as chairman. In the general field of the biological sciences, exclusive of the medical sciences, selections of postdoctoral fellows will be made by a board under the chairmanship of Dr. R. G. Gustavson, Chancellor of the University of Nebraska. For the selection of postdoctoral fellows in the medical sciences, a board has been set up under the chairmanship of Dr. Homer W. Smith, Professor of Physiology, College of Medicine, New York University.

The program provides for two groups of fellows in the predoctoral field. One group of fellows will work in the biological and basic medical sciences including applied biophysics relating to the measurement and control of radiation hazards and the effect of radiation upon health. Selections will be made by a board under the chairmanship of Dr. Douglas Whitaker, Professor of Biology, and Dean of the School of Biological Sciences, Stanford University. Another group of predoctoral fellows will be selected for study and research in the general field of the physical sciences. Selections will be made by a board under the chairmanship of Dr. Henry A. Barton, Director of the American Institute of Physics.

Awards will be made for the academic year 1948–49. The program is administered by the National Research Council. Further information can be secured by writing to the Fellowship Office, National Research Council, 2101 Constitution Avenue, Washington 25, D. C.

POSITIONS AVAILABLE

ELECTROCHEMICAL ENGINEER, thoroughly familar with the manufacture and production of dry cell flashlight batteries to take charge of new battery manufacturing plant in Colombia, South America. Reply to Box A-199, The Electrochemical Society, Inc., 235 West 102nd St., New York 25, N. Y.

CORROSION ENGINEER, extensive industrial experience in physical metallurgy, corrosion, and materials of construction in the chemical industry required. Location southwest. Reply to Box A-200, The Electrochemical Society, Inc., 235 West 102nd St., New York 25, N. Y.

ELECTROCHEMIST, qualified, responsible, for permanent position with established eastern dry battery manufacturer. Development and manufacturing experience in dry batteries preferred. Salary commensurate with responsibility. All replies to be held confidential. Reply to Box A-201, The Electrochemical Society, Inc., 235 West 102nd St., New York 25, N. Y.

POSITIONS WANTED

ELECTROCHEMIST, broad experience in research, development process control, industrial materials engineering, and finishing methods. Metropolitan New York or New England area preferred. Reply to Box 317, The Electrochemical Society, Inc., 235 West 102nd St., New York 25, N. Y.

CHEMICAL ENGINEER, age 27, experienced in organic and inorganic metal finishing. Seeks position in sales or research department of progressive firm. Reply to Box 318, The Electrochemical Society, Inc., 235 West 102nd St., New York 25, N. Y.

METALLURGIST, B. S. (Chem.), age 36, post-graduate work in metallurgy, desires position in production and refining of non-ferrous metals. Experienced in process development applying furnace, electrolytic, and leaching methods to production and refining of copper, lead, silver, tin, cadmium, zinc, and other metals. Location secondary. Reply to Box 319, The Electrochemical Society, Inc., 235 West 102nd St., New York 25, N. Y.

CHEMICAL ENGINEER, 10 years experience in the development and operation of automatic and continuous plating equipment. Desires responsible position comprising technical development of production processes, special techniques, and essential equipment. Located in Ohio, Pacific Northwest preferred. Reply to Box 320, The Electrochemical Society, Inc., 235 West 102nd St., New York 25, N. Y.

NEW MEMBERS

At the meeting of the Executive Committee held on April 2, 1948, at the office of The Electrochemical Society, Inc., 235 West 102nd St., New York City, the following were elected to membership:

WILLIAM HUGH BARKLEY, Chem. Engineer, Champion Fibre & Paper Co., mailing add: Chipmunk Cottage, Albemarle Park, Asheville, N. C. (Theoretical Electrochemistry, Corrosion, Alkali and Chlorine, Electrodeposition, Power)

FRANK HERBERT CHAPMAN, Res. Engineer, Consolidated Mining & Smelting Co., mailing add: P. O. Box 18, Trail, B. C., Canada (Theoretical Electrochemistry, Electrodeposition, Electrothermics)

HENRY PHILIP DEWITT, 1167 Longfellow Street, Detroit 2, Mich. (Theoretical Electrochemistry, Corrosion, Electrodeposition)

HARRY LANDIS EBERLY, Chem. Engineer, Western Electric Co., 555 Union Blvd., Allentown, Pa. (Corrosion, Electrodeposition)

GEORGE CROSBIE FLOYD, Thomas Steel Co., Delaware Ave., Warren, Ohio (Theoretical Electrochemistry, Corrosion, Electrodeposition)

ELMER LEROY HAGERTY, Kirsch Co., mailing add: Box 95, White Pigeon, Mich. (Electrodeposition)

KARL S. HAGIUS, Colorado Interstate Gas Co., mailing add: P. O. Box 1067, Colo. Spgs., Colo. (Corrosion, Electronics)

MARCUS RANKIN HATFIELD, National Carbon Co., mailing add: 12531 Clifton Blvd., Lakewood 7, Ohio (Theoretical Electrochemistry, Batteries)

ARTHUR HIXON, Res. Chem., J. Kreisler Corp., mailing add: 4455 Broadway, New York 33, N. Y. (Theoretical Electrochemistry, Organic Electrochemistry, Corrosion, Alkali

& Chlorine, Electrodeposition, Electrothermics, Electronics)

ALVIN E. MCDOUGALL, Westvaco Chlorine Products Corp., South Charleston 3, West Va. (Alkali & Chlorine, Power)

BRUCE G. NANNEY, Champion Fibre & Paper Co., mailing add: 37 Pharr St., Canton, N. C. (Corrosion, Alkali & Chlorine, Power)

PETER CARL PERRY, Timbrol Ltd., mailing add: 18 Stanhope Rd., Killara New South Wales, Australia (Alkali & Chlorine, Organic Electrochemistry, Corrosion)

KEMPTON HARRIES ROLL, Lead Industries Ass'n., 420 Lexington Ave., New York 17, N. Y. (Batteries, Corrosion, Electrodeposition)

JACQUES J. M. ROOS, William Smit en Co's Transformatorenfabriek, N. V., Nijmegen, Holland (Electrothermics, Electronics, Dielectrics)

MYER SHAPIRO, Gillette Safety Razor Co., mailing add: 76 Peterborough St., Boston 15, Mass. (Electrodeposition)

HAROLD B. STALEY, Penn. Salt Manufacturing Co., mailing add: 657 Tyson Ave., Ardsley, Pa. (Theoretical Electrochemistry, Electronics)

WILFRID HENRY STOLL, Canadian National Carbon Co., Ltd., 805 Davenport Rd., Toronto, Canada (Batteries)

GARRETT WILLIAM THIESSEN, Prof. of Chem., Monmouth Coll., mailing add: 408 N. 10 St., Monmouth, Ill. (Theoretical Electrochemistry, Organic Electrochemistry, Batteries)

HAROLD ALFRED TIMM, Dominion Magnesium, Ltd., Haley, Ontario, Canada, (Theoretical Electrochemistry, Organic Electrochemistry, Batteries, Corrosion, Electrodeposition, Electrothermics, Power)

BOOK REVIEWS

GERMAN ELECTROPLATING INDUSTRY by G. E. Gardam. Published by Mapleton House, Publishers, 5415 Seventeenth Avenue, Brooklyn 4, N. Y. 72 pages, $5.00.

This report by Dr. Gardam describes the companies and the kind of electroplating done before and during the war. There are brief comments on the plating techniques in comparison with United Kingdom methods and with methods in the U. S. A., as far as Dr. Gardam was acquainted with the latter.

The outstanding impression is that German electroplating is much less technically advanced than that in the U. S. A. Only a small amount of research is done by groups having no interest in applications or production. The latter is done by artisans who employ "rule-of-thumb" control methods in manually operated plants for the most part.

The American plater will find little in the way of new knowledge applicable to his industrial operations and techniques. The plating methods were mostly handled as proprietary or ready mixed solutions supplied by a few firms. Plating rate and methods were essentially the same as those in general use 10 to 20 years ago in America.

Electropolishing was employed for smoothening working parts of gun mechanism. The perchloric—acetic solutions were used with several explosions resulting.

Dr. Gardam's investigation disclosed a commercial process for "currentless plating" of cadmium on steel and aluminum alloys.

Of interest to the military and others concerned with wartime substitutions was a practice of using a hard (280–400 Vickers) bronze plate (3 to 10 per cent tin in copper) in place of very critical nickel on parts such as plug cocks, valves, marine propellers, rings, and other steel articles. These were bronze plated in a cyanide bath at a speed equivalent to that for bright nickel plating, and were then plated with chromium.

Some small arms ammunition was zinc plated (0.0001 to 0.0003 inch), and passivated in dilute phosphoric acid solution, principally for corrosion resistance, but also with benefit to wear of barrel bores. Much materiel was chromium plated. Large numbers of breech mechanisms and barrel bores were chromium plated and used to fire unplated steel bullets. This chromium plating was similar to procedures familiar to American platers.

Except for specifications covering zinc plating, no organized system was found for regulating workmanship or quality of plate. With a few exceptions, thicknesses were less and current densities lower than for general practice in America. Filtration, particularly, was almost unheard of.

Charles L. Faust
W. H. Safranek

ELECTROCHEMICAL ANALYSIS WITH GRADED CATHODE POTENTIAL CONTROL by Harvey Diehl. Published by G. Frederick Smith Chemical Company, 867 McKinley Avenue, Columbus, Ohio. 56 pages, $1.00 (May be obtained from the publisher in paper binding gratis).

This is another in the series of booklets published by the G. Frederick Smith Chemical Company for the purpose of stimulating interest in certain types of chemical analysis. This sort of advertising is useful to the analyst for these booklets are always well written by authorities in the fields described. An attempt is usually made to provide a rather complete survey of the literature and to give actual instructions of the operations of instruments and the details of the analyses. The present book does not pretend to be a reference text on electrochemical analysis. It contains a brief account of the theory and practice of electroanalysis with graded cathode potential control, a description of an apparatus designed for automatic control of the cathode potential during electroanalysis, and a few typical examples of published methods using graded cathode control.

C. L. Luke

PATENTS OF INTEREST TO ELECTROCHEMISTS

Selected by Fred. W. Dodson, Chairman of the Patent Committee, from the Official Gazette

February 10, 1948

Franks, R., 2,435,624, Weather Resistant Steel and Articles

Grandstaff, O. D., 2,435,681, Current Rectifying System

Solomon, Myer, deceased, by Solomon, N. W., administratrix, 2,435,700, Process of Electrolytically Producing Azo Dyes on A Fibrous Sheet Material and The Fibrous Sheet Material For Said Process

Fusco, A. J., and Bleiweis, J. L., 2,435,714, Electrochemical Salvaging Method

Coulson, S., 2,435,872, Method of Electroplating Cylinders

February 17, 1948

Jernstedt, G. W., 2,435,967, Bright Alloy Plating

MacTaggart, A. B., and Thomson, G. J., 2,435,973, Method of and Means for Providing Cathodic Protection of Metallic Structures

Taylor, I. M., deceased, by Henry, I., administrator, 2,435,986, Antifouling Device

Krasnow, S., and Curtiss, L. F., 2,436,008, Signalling System for Radioactive Well Logging

Lebedeff, Y. E., 2,436,010, Process for Recovering Metallic Tin and Antimony-Tin Alloy from SB-SN-AS Bearing Materials

Pugh, M. L., 2,436,057, Battery Charging Apparatus

Weller, B. L., 2,436,084, Ionization Chamber

Barrick, P. L., and Christ, R. E., 2,436,135, Halogenation of Fluorinated Compounds

Schmidling, G. T., 2,436,182, Phosphorescent Resin Composition

Phillips, H. P., 2,436,227, Method of Forming Piston Ring Elements of Ribbon Steel

Benner, H. L., and Bair, R.R., 2,436,244, Metalworking and Stripping-Plating Process

Hindall, A. L., 2,436,299, Storage Battery Plate Paste Expander

Lum, J. C., and Jernstedt, G. W., 2,436,316, Bright Alloy Plating

Sconce, J. S., and Johnson, A. N., 2,436,366, Processes for Chlorination of Hydrocarbons

February 24, 1948

Deibel, C. P., deceased; Mertes, C. N., and Gray, L. A., 2,436,382, Dry Cell Battery of the Flat Type

Wilson, H. D., 2,436,465, Underwater Battery Vent Plug

Du Rose, A. H., 2,436,690, Acid Chloride-Fluoride Bath for Nickel Plating

March 2, 1948

Schulein, J., 2,436,940, Method of Regenerating Anodizing Baths

Warner, A. R., 2,437,009, Illuminated Sign

Woodbridge, J. L., 2,437,145, Nonspill Vent for Storage Batteries

March 9, 1948

Ohl, R. S., 2,437,269, Translating Device and Method of Making It

Thompson, L. E., and Jenkins, A., 2,437,336, Alternating Electric Current Rectifier

Tucker, W. M., 2,437,409, Activating and Electroplating Stainless Steel

Dunham, L. S., 2,437,422, Protective Gas-Permeable Container for Air-Depolarized Cells

Chemicals from Coal

Products derived from coal have always been important raw materials for the chemical industry. Many aliphatic synthetic compounds have been based on coke via water gas or carbide reactions or on the simple hydrocarbon benzene, while coal tar itself has until recently been the chief raw material for a great diversity of simple and complex aromatic structures.

With the coming production of liquid fuels from coal, our vast coal resources will become an increasingly important source of chemicals. The direct hydrogenation of coal can greatly augment, if necessary, our present supply of basic coal tar chemicals such as benzene, naphthalene, and the tar bases and tar acids, while production of motor fuels by the indirect reaction of carbon monoxide and hydrogen necessarily entails the making of large amounts of aliphatic alcohols, simple acids, esters, and high molecular weight waxes.

Other processes based on direct reactions on coal may also prove of increasing importance to the chemical industry. Much of the fundamental knowledge on these developments has been supplied by the notable researches of the Coal Research Laboratory of the Carnegie Institute of Technology.

Coal reacts vigorously with chlorine to yield a small proportion of chlorinated hydrocarbons and a complex mixture of cyclic compounds. While it is difficult to resolve this group of condensed ring structures, it is possible that future work may suggest practical methods for obtaining valuable intermediates from this source.

A more promising direct process for obtaining chemicals from coal is that of controlled oxidation. If a suspension of powdered coal in aqueous alkali is subjected to the action of oxygen at elevated temperatures and pressures, there is produced a mixture of water soluble polycarboxylic acids of varying degrees of complexity. Containing several carboxylic groups per molecule, these products should be of interest in the high polymer field and find application as plasticizers and in the synthesis of resins.

The industrial development of chemicals from coal will need the cooperation of the electrochemical industry. Alkali and chlorine will be required and electrothermic equipment and electroorganic chemical processes should play essential roles. Finally, electrochemical instrumentation will be required for the control of the many intricate chemical operations which will be involved in the new industry.

R. M. B.

News Notes

REPORT ON COLUMBUS CONVENTION

Three hundred and thirty-one members and guests of The Electrochemical Society convened in Columbus, April 14th to 17th, for the ninety-third semi-annual meeting of the organization; this registration exceeded by about 100 that of April, 1939 when Columbus played host to the Society for the first time.

The Hon. Thomas J. Herbert, Governor of Ohio, briefly addressed the assembly at the formal opening of the convention on the morning of April 15th. Introductory remarks by President G. W. Heise followed. Presiding over the morning session on Corrosion was Dr. H. J. McDonald who skillfully guided the presentation and discussion of the ten papers included in the symposium.

A luncheon in the ballroom of the Deshler-Wallick at noon was well attended and an informative talk, "The Case for Co-operatives," proved interesting to those present.

Mr. Heise conducted the afternoon discussion which dealt with a half dozen presentations on topics of general electrochemical interest.

At 7:00 P.M. a reception was held for President and Mrs. Heise and, an hour later, the Annual Banquet was served in the ballroom. At this time, presentation was made of the Young Author's Prize to Henry Leidheiser, Jr., and Austin E. Hardy formally received the Turner Book Award. Mr. Heise selected for his Presidential Address, "The History of the Primary Cell." In his talk, President Heise traced the development of the cell from the humble (and perhaps amazing) experiments of one hundred and more years ago down through the times to the present day in which enormous production and extreme compactness of these cells has become a realization of the primary battery industry. The address, profusely illustrated with slides, was warmly received. Later, music for dancing was provided and refreshments were served.

HENRY LEIDHEISER, JR. RECEIVES YOUNG AUTHOR'S PRIZE FROM G. W. HEISE

Dr. Peter Pringsheim, of Chicago's Argonne National Laboratory, the keynote speaker at Friday morning's technical session on Luminescence, chose as his subject, "Some Unsettled Problems in the Field of Crystal Phosphorescence." Dr. E F. Lowry introduced the eight speakers for the papers on the program. This was a very successful sym-

posium and many of those present met in the afternoon for further discussion of the developments described in the morning presentations.

On Friday, the ladies enjoyed a sightseeing tour and luncheon while the men were guided in an inspection trip of Battelle Memorial Institute and Ohio State University. At Battelle, they delivered a short speech on the history and development of rare metals and introduced the authors featured on the morning program. Many of the papers in this session are published in this issue of the Journal. The film, "The Recovery of Rare Metals," was an especially fine review of the problems involved in the extraction of such metals

F. M. Turner Presenting Book Award to Austin E. Hardy

witnessed the electrochemical, metallurgical, and ceramic research laboratories in operation and were shown various exhibits of rare metals processes and unusual corrosion testing equipment. At Ohio State University, they were conducted through the famous Engineering Experiment Station and had occasion to observe the facilities for corrosion, ceramics, and cryogenic research. The trip was highly interesting and informative to those who went. Arrangements for the tours and transportation to and from the laboratories were secured by Mr. C. J. Slunder of the Local Committee.

That evening, a sumptuous buffet supper in the Hall of Mirrors and entertainment in which the guests participated successfully climaxed the efforts of J. Homer Winkler, Chairman of the Entertainment Committee.

The final day of the convention contained another of the interesting symposia, "Rare Metals." Dr. J. W. Marden as gallium, germanium, and indium from native ores.

The symposium concluded in the afternoon and a session on Electrothermics was conducted by Dr. J. D. Sullivan lasting until the convention's adjournment at 4:00 P. M. The meeting ended with words of congratulation expressed to the Local Committee for the excellent manner in which all arrangements had been performed. In addition to those already mentioned, praise was directed to Vice Chairman Fred W. Fink, to A. E. Pavlish, P. D. Miller, R. I. Jaffee, C. A. Snavely, and A. B. Tripler for their efforts on the Hotel and Registration Committee; to R. M. Schaffert as Chairman of the Publicity Committee; to the wives of the aforementioned gentlemen for providing a splendid program for the visiting ladies; and to Dr. Clyde Williams, Chairman of the Finance Committee and Honorary Chairman of the entire Convention Committee.

SECOND ANNUAL CONFERENCE ON BATTERY RESEARCH AND DEVELOPMENT

The results of the battery research and development investigations, sponsored at various universities and industrial research organizations by the U. S. Army Signal Corps, were presented to over 150 representatives of the primary and secondary battery industry at the Second Annual Conference on Battery Research and Development held at Red Bank, N. J. on the 30th and 31st of March under the direction of the Battery Branch, Signal Corps Engineering Laboratories, Fort Monmouth, New Jersey. Many members of the Battery Division of The Electrochemical Society attended this Conference and it is expected that some of the work described, when completed, will be published in the Journal.

For the past two years, the Signal Corps has contracted with many universities and industrial research organizations to conduct research of a fundamental nature leading to the improvement of the performance of primary and secondary batteries. This information will ultimately lead to the development of batteries capable of satisfactory operation under the most severe military operational conditions. Included in these investigations are studies leading to the development of low temperature batteries, batteries using magnesium as the anode material, more efficient depolarizers and the study of the properties of depolarizing oxides, the improvement of the performance of lead-acid storage batteries, and the investigation of new electrochemical combinations for use as battery power supplies. Annually, the battery industry is invited to attend these conferences to assist in the further planning of research and to obtain the latest information regarding research trends in their particular fields. This research data thus disseminated will prove mutually beneficial to both the government and the battery industry and will lead to the development of improved commercial and military batteries.

MANGANESE DIOXIDE REPORTS

At the morning session on March 30th, two papers on manganese dioxide were presented. Dr. G. H. Kissin of the Georgia School of Technology discussed the progress on the development of an electrolytic method for the production of a battery grade manganese dioxide ore. Materials produced have been characterized by the electron microscope, by electron and X-ray diffraction techniques, by chemical methods, and by determining the performance of batteries constructed using these ores. The products exhibited typical gamma patterns and the results on initial capacity tests are superior to those obtained with natural ores. The shelf life characteristics of the synthetic ores are still variable but are encouraging. Dr. P. W. Selwood, of the Northwestern University, discussed the applicability of magnetic methods to the study of manganese oxide structures. He compared the magnetic properties of "pure manganese dioxide" with those of various other oxides and modifications of oxides and described the apparent effects of water and non-stoichiometry as well as the influence of small amounts of iron on the magnetic properties. The use of supported oxides as the guide to structural studies was also described.

The progress on the development of a non-reserve dry cell capable of operation at low temperatures was reported by Dr. C. K. Morehouse of Olin Industries. Experimental "D" size dry cells were prepared by Dr. Morehouse and his coworkers using a zinc can anode, an electrolyte consisting of low temperature formulation, a manganese dioxide-acetylene black mixture as the cathodic material, and a paste separator consisting of starch and flour gels. These cells showed promising service possibilities at low temperatures.

INVESTIGATIONS OF NEW ELECTROCHEMICAL SYSTEMS

The afternoon session was devoted to reports on the investigations leading to the development of new electrochemical systems for use as battery power supplies. Dr. H. J. McDonald of the Illinois Institute of Technology discussed experiments on cells using liquid sulfur dioxide, liquid ammonia, and other non-aqueous liquids as electrolyte solvents. These electrolytes permit the use of sodium and other materials high in the electrochemical series as anodes, resulting in cell voltages in the order of 2½ to 3 volts. The results of the investigations on the properties of electrolytes

and electrochemical couples suitable for operation as cells at low temperatures were described by Dr. A. B. Garrett of Ohio State University. Several acid systems were reported as promising for low temperature operations but Dr. Garrett concluded that, as yet, no system is know that will have enough potential activity at low temperatures to be usable in a cell and, at the same time, have a low enough activity at room temperature to give good shelf life. This problem may be solved with the use of proper inhibitors and cell design. The physical constants, such as density, viscosity, conductivity, and dielectric constant at various temperatures of organic solutions, found promising as electrolytes for low temperature batteries were presented by Dr. G. R. Leader of the University of Kentucky. Dr. W. C. Vosburgh, Duke University, reported on the results of studies on the polarization in a number of electrochemical systems. This was studied by measurement of the current passed between two electrodes and the potential difference between one of them and an auxiliary calomel electrode.

The progress in development of a dry cell using magnesium as the anodic material was discussed by Dr. R. C. Kirk of the Dow Chemical Company during the sessions held on March 31st. He reported the design of a cell using a magnesium can (constructed of FS-1 alloy), a flour-starch paste with strontium bromide electrolyte, and African manganese dioxide with Shawinigan black as the cathode. The cell is equivalent in watt-hours to the standard zinc dry cells on initial capacity. Results of delayed capacity tests on the early cells were reported as unsatisfactory but later cells constructed with suitable inhibitors give promise of considerably improved shelf life characteristics.

The remainder of the conference was devoted to discussing the results of the investigations on secondary batteries. Dr. G. L. Clark reported on the results of his investigations to improve the low temperature performance of lead-acid storage batteries. X-ray methods have been devised for evaluating the porosity of plates as the function of temperature during formation or charging. Dr. Clark observed that the porosity in the negative plates decreases almost linearly over the temperature range of 100°F. to 0°F. and more rapidly from 0°F. to −65°F. This factor which is apparently unfavorable for capacity is, however, more than offset by the formation at 0°F. of small distorted lead crystals having large total surface area with high surface activities and heats of solution. Regarding the positive plate, it was reported that the effects of decreased temperature on porosities, densities, and activities are nearly negligible. Mr. Ritchie, of the Eagle-Picher Company, indicated the difficulties involved in making precise studies of the lead oxides. He outlined a semi-micro analytical method for precisely determining the amount of lead in a high purity, high lead-content oxide. The necessity for getting a clear picture of the lead-oxygen system is found in the fact that changes in the method of manufacturing the lead oxides may have large effects on the performance characteristics of batteries made from these oxides. The influence of impurities on the crystal structures is well recognized and hence the great importance of having reference standards as free from impurities as is possible. The study of commercial lead oxides, with the knowledge gained from the very pure materials, will enable a number of factors to be evaluated, and it is hoped that eventually this will lead to the evaluation of the storage battery performance of any commercial lead oxide on the basis of its chemical analysis, diffraction pattern, and particle size determination.

NOTE TO AUTHORS

It is imperative that manuscripts to be presented at the Fall Meeting of the Society be submitted to the office of the Secretary at the earliest possible date. Each manuscript received is carefully reviewed, edited, and processed for the printer and consequently, because of the time element and copy deadlines, papers received at the last minute cannot be readily considered for publication.

CATHODIC PROTECTION PAPERS TO BE PUBLISHED

The papers presented at the Cathodic Protection Symposium held last December in Pittsburgh, Pa., will be published jointly by The Electrochemical Society and the National Association of Corrosion Engineers. The date of publication is tentatively November 1, 1948. The manuscripts will be edited and assembled in an inexpensive bound volume.

INDUSTRIAL PROPERTY

DEAN LAURENCE

Industrial property is probably the least understood form of property known to the law. To understand "property," an examination should be made of its history. It began as booty held as a trophy of a successful raid. This early form of ownership, involving acquisition by simple seizure and conversion, began to pass into the subsequent stage of an incipient organization of industry on the basis of private property as in slaves. Gradually, as industrial activity displaced predatory activity in everyday life and in men's habits of thought, accumulated goods, money, and legal rights gradually replaced trophies of predatory exploits. With the growth of settled industry, therefore, the possession of wealth gained in relative importance and effectiveness as a customary basis of repute and esteem. The dominant incentive to ownership of property has, from the outset, been the apparent distinction attaching to wealth and, save temporarily and by exception, no other motive has usurped its primacy at any later stage of the development.

Monopolies constitute an interference with the common law right possessed by every member of the community to carry on any trade or business he chooses in such a manner as he thinks most desirable in his own interests. Generally, there is odium attached to the term "monopoly." If a man is to be given a monopoly, which is a right, then the maxim that every right connotes an obligation acquires force. No one can lawfully interfere with another in the free exercise of his trade or business unless some just cause or excuse for such interference exists. A monopoly is a right granted by the executive authority at the expense and to the prejudice of the community except the grantee. The law of industrial property is not concerned with such kinds of monopolies. When a seller of goods selects a trademark, it must be something not used before by others. He cannot preempt that which is already known. When an inventor is rewarded by a patent for his disclosure of a certain thing to the public, his patent claims must read on that which is novel and inventive, in short, something which the public did not before him possess. Industrial property, then, does not involve a derogation from the common law right in virtue of which any member of the community may exercise any trade or business he pleases. By nature, it represents an addition to the sum of human knowledge, welfare, and possibilities for mental and physical satisfaction.

In summary, industrial property consists of the new things contributing to human comfort on which businesses are founded with a view toward supplying the things to the public. But businesses are, in the beginning, ventures; if the adventurer cannot see a potential reward, there will be no venture. The patent system is the most equitable mode of rewarding an adventurer yet devised by man.

The research director of a well-known chemical company has asked why his company should spend any money on patents. Any patent attorney would find it easy to answer this. However, most attorneys will not go very far before taking refuge in the excuse that the language of craftsmen is unintelligible to those untutored in the craft. Such an excuse may cover with a semblance of respectability, an otherwise ignominous retreat. It does not satisfy. To provide a satisfactory answer it is necessary to make certain assumptions.

I shall assume that a chemist is no different from any other man in that he can be induced to continued labor only by hope of reward or fear of punishment; that he is an advocate of an economic system which holds that each man is entitled to enjoy the fruits of his honest labor, whether physical or mental, to the exclusion of others; and that he believes the affairs of men ought to be governed with that serene and impartial uniformity which is of the essence of the idea of law.

Now let us apply these principles to the subject of inventions. In the scientific world as in the business world, I have yet to observe the man whose direct, impelling motive to any action did not derive from the economic advantage which he, as the beneficiary, expected would accrue to himself from his action. If you want new ideas, new discoveries, hold out a desirable reward, and, if he possibly can, the scientist will

then, and only then, produce. There may be some who profess that, as men of pure science, they will work without hope of reward. Despite assertions that great scientific minds will work and strive without thought or hope of reward, the solid fact remains that, in essence, the mainspring of human activity is self-interest. Inventions are pressed to conclusion by the hope of material reward far more than by the hope of posterity's acclaim.

How can we best hold out a reward commensurate with the value of any possible achievement and assure a man that society will not avail itself of his creative efforts without paying him his due? If a man wanders into the hills and emerges with a sack of gold or a handful of diamonds, others may envy and scheme to turn his good fortune to their account. In any but a so-called communistic state, the exclusive title in that which the aforesaid fortunate fellow has gotten by chance discovery will be protected by law. The final cause of law is the welfare of society. If the chance discoverer of golden nuggets be adjudged entitled to protection in his gain, ought not another man, who, by untiring toil and sheer mental effort, creates intellectual property before unknown, to be protected in the exclusive enjoyment of that which he has thus created? Is not the welfare of society equally served thereby? One of the most fundamental interests is that law shall be uniform and impartial.

The draftsman of the Constitution incorporated the provision investing Congress with the power to enact the necessary legislation "to promote the progress of science and the useful arts, by securing for limited times to authors and inventors the exclusive right to their respective writings and discoveries." But the present statutory enactments, it is submitted, are nothing more than the modern expression and acceptance of rights long since established and rendered necessary in a civilized state by the exigencies of human circumstance. The system as we see it in operation today is not the result of inspired thinking, but is a dictate of historical necessity.

What is the object of the patent system? The Constitution answers: "To promote the progress of science and the useful arts." Now any promotional venture will only be undertaken if there is an opportunity for a reward. The drafters of the Constitution could have formulated a method of reward, greater or lesser in elaboration, involving the immediate payment directly by the government to inventors for making public disclosure of their respective inventions. Wisely, this was not attempted. Those in the management of even small companies who have attempted to devise an immediate direct reward system have generally given it up as a bad job. The Constitutionalists devised instead the best possible system for reward. They said, putting it in the vernacular, "If you will let the public in on your idea and how to use it, the government will secure to you for a limited time the sole right to make and to sell and to use your mousetrap. If the public likes your product and you make a million, bless you for creating a new source of taxable income. If the public doesn't cotton to your contraption, we hope you will try again and no damage has been done the public anyway." The reward can be directly proportional to the contribution, under the Constitution.

There is a duty upon an inventor, devolving upon his assignee, to disclose fully any particular invention sought to be patented. Again, the law protects the inventor while he determines the issue of the size of his patent. Pending applications are preserved in secrecy. When the shouting and the fury has died away, the inventor decides whether the patent he can get is big enough to suit him, and, if he prefers to attempt to keep his invention secret, he doesn't pay the final fee to issue the patent and the public is, directly, no wiser.

Invention consists, fundamentally, in the isolation and solution of problems. The presence of invention is made evident by the failure of the prior art to present the complete solution of the totality of problems involved. The measure of the invention is provided by the character and extent of the problem and the manner of solution.

Isolation of the problem is a prerequisite to the formulation of the solution or solutions. If the art carried no suggestion of the problems, it carried no solutions, and the invention is of basic scope. If it carries a partial solution, the missing problems must be isolated from those solved by the known solution, antecedent to development of a final, complete solution; and, basically, such final solution must deal with both the known and the isolated problems in their relation one to

the other, rather than individually. If the art fails to suggest any solution—even broadly—of the problems solved, the invention is of basic scope.

The enunciation by our Supreme Court of the "flash of genius" doctrine, as a measure in determining the extent of protection to be accorded any particular invention or discovery, is not disturbing. I define "genius" as "the appreciation of significance" and "monopoly" in a patent sense as "the exclusive right for a limited time to enjoy the fruits of a product of genius not previously know or readily deducible from the previously known."

I think the Patent Office has three basic functions: First, to see that the inventor actually gives the public a clear disclosure of his invention in such a way that it may use it; second, to claim the invention so that it may be readily ascertained just what are its limits within which an imitator cannot enter; and, third, to measure the degree of novelty the inventor has claimed. The public will measure the value of that degree of novelty.

It is the natural instinct of the business man to get along with what is good enough as long as it satisfies the public demand, and to take up new and improved things only when there is a public clamor for them. This is natural because the process of evolution in the industrial arts necessitates the waste of discarding the old and the obsolete. The inventor is the evolutionary force, while the business instinct of the manufacturer who puts his invention to use is an element of inertia against which the inventor must continually struggle.

It is hardly less important to encourage inventors to make inventions than it is to encourage business men and the public to take up inventions and put them to use. In a company offering a product generally satisfactory for its intended purpose, there is a pronounced tendency to exhibit a certain amount of hesitation before it junks its investment in manufacturing equipment and undertakes to make the shiny new product of the inventor in research.

One of the functions of the patent system and one of the reasons why the research director should spend his company's money is to tide the company over the period when it cannot economically, as a matter of good business practice, manufacture the newly discovered product which it will eventually market. It is necessary to keep others from appropriating the fruits of expensive research before a company is in a position to use them. It may even be called insurance.

Another reason why the research director should spend his company's money on patents is that, under our present law, an inventor is entitled to a patent. If he procures the same, then he is entitled to avail himself of all lawful remedies against those who seek to infringe his grant.

A third reason is this: The sole and tough excuse for the existence of a business venture is to show a profit. However, there is a larger duty devolving upon those who conduct our industrial organizations. That duty, in part, is to see that succeeding generations shall gain something from the present generation. More money could be gotten by the present generation of business men if all research were stopped for ten or fifteen years. More money could be gotten by many companies if a compound wherein the employees live and the manufacturing operations are carried on could be established, thereby to preclude the loss of any knowledge through the departure of employees and the leakage of know-how. These things are not generally thought of as feasible or desirable. It is far better for the welfare of society, which includes the welfare of companies, that technical information be freely exchanged. A chemist rarely gives more than he gets, over the long haul of his scientific lifetime. And he ought to give freely. The work of every one of the research director's men is grounded in the published work of scientists long dead, his teachers, and his contemporaries. The patent system, properly used, tends toward an elimination of the necessity for secret processes. There is never any possibility of stepping backwards in the progress of knowledge, no matter how small the improvement. Each invention is inevitably the seed of future inventions.

It is a duty upon each company to inform the public fully of the nature of each of its inventions. It is the duty of the public to recognize that, in return for such disclosure, the company is entitled to the right of exclusive use for a limited period. And it is the duty of the Patent Office and the Courts to see that such right is granted and protected from infringers. Bar such protection to research results and we return to secret processes and contravene the "promotion of progress" clause of the Constitution.

DIVISION NEWS

Electrothermic Division

A. E. Pavlish, *Secretary-Treasurer*
Battelle Memorial Institute
Columbus, Ohio

The Electrothermic Division held a business meeting and election of officers on Saturday afternoon, April 17th, at the Columbus Meeting of the Society. C. P. Zirgiebel, of Victor Chemical Works in Mt. Pleasant, Tenn., former Secretary-Treasurer of the Division, was elected Chairman; Julian Glasser, of the Armour Research Foundation in Chicago, Ill., became the new Vice Chairman; and A. E. Pavlish, of Battelle Memorial Institute in Columbus, was elected Secretary-Treasurer of the Division.

Theoretical Electrochemistry Division

W. L. Haden, *Secretary-Treasurer*
Pittsburgh Plate Glass Company
Barberton, Ohio

Dr. George Glockler, Head of the Department of Chemistry and Chemical Engineering at The State University of Iowa in Iowa City, Iowa, has recently been chosen by the Board of Directors of the Society the new Chairman of the General and Theoretical Electrochemistry Division. Dr. Glockler, an active member of the Society, is the author of several papers which have appeared in the Transactions. Keenly interested in theoretical electrochemistry, he is now making the arrangments for a symposium on General and Theoretical Electrochemistry which is being scheduled for the Spring Meeting of 1949 to be held in Philadelphia.

SECTION NEWS

Cleveland Section

Charles Sanborn, *Secretary-Treasurer*
2231 Wrenford Road
University Heights 18, Ohio

Fourteen members of the Cleveland Section met on the 13th of April for lunch at the General Electric Company, Nela Park. Later they were joined by other members for an interesting plant inspection trip at Willard Storage Battery Company.

Niagara Falls Section

M. S. Kircher, *Secretary-Treasurer*
Hooker Electrochemical Company
Niagara Falls, New York

A joint meeting of The Niagara Falls Section of the Electrochemical Society and the Western New York Section of the American Chemical Society was held on February 17th at the Prospect House in Niagara Falls. The highlights of the meeting were talks by Dr. William Julian King, Director of the Sibley School of Engineering and Mr. George W. Heise, President of The Electrochemical Society. This annual joint meeting and address by the President has become an annual custom at Niagara and is considered the high point of their season's calendar; this years meeting, both in interest and attendance, was outstanding.

Dr. King's address, the character of which was not entirely reflected in the title, "Personal and Professional Problems of Engineers," was a sincere and thought-provoking plea to technical people to apply their intelligence, ability, methods, and energy to problems of greater significance. In stressing this plea, Dr. King gave his conception of what the effect on society would be if the technical energies spent in the development of such things as jet engines could be spent instead on working out the problems of world peace. Dr. King feels that the technically trained mind is particularly qualified to engage in a study of the yet undeveloped science of national relationships.

Mr. Heise, in his talk, "Some Applications of Porous Carbon Electrodes," reviewed several applications of these electrodes which are of particular interest to the industrial electrochemist; Mr. Heise and his coworkers at National Carbon Company have spent several years doing research in this field.

The air cell battery is one of the better known applications of porous carbon because of its extensive use during the war, and Mr. Heise explained that the war had been instrumental in holding up their work on the development of other uses of porous carbon. He pointed out, further, that porous electrodes, through which reactants may be admitted to, or products withdrawn from, a cell, have attractive possibilities in that they offer a means for the elimination of diaphragms, reduction of power requirements, and continuous operation at high

effective current concentrations of electrode reactions which normally can be carried on only by batch methods. Through the use of porous electrodes, maximum concentration of reactant at the active electrode surface is insured, polarization is reduced to a minimum, permissible current densities are increased, and concentrations at which operations can effectively be conducted may be substantially lowered.

One of the most spectacular of the experiments carried out with porous electrodes was the oxidation of arsenate. In this experiment, current efficiencies of 160–165 per cent were obtained, whereas, with solid electrodes, efficiencies considerably below 100 per cent are obtained. The explanation of this curious fact is that, with air depolarization of the cathode, oxidation of the arsenite takes place at the cathode as well as at the anode.

Other applications of porous carbon electrodes discussed by Mr. Heise are oxidation of manganate to permanganate, production of electrolytic iron, electrowinning of copper, reduction of P-nitraniline to P-phenylenediamine, and the electrolysis of sodium chloride.

Much of the work discussed by Mr. Heise has been published in the Transactions of The Electrochemical Society **76**, 147 (1939) and **77**, 411 (1940). Another paper on this subject is planned for presentation at the Symposium on Electrolytic Production of Metals at the meeting to be held in October, 1948.

NEW SOUTHERN CALIFORNIA SECTION

Several members of the Society, including E. A. Calderon and Will Baughman, have been instrumental in the organization of a new Local Section of the Society. Feeling that a significant number of members are located in the Los Angeles area, these men, with the assistance of R. B. Cox who helped organize and write the by-laws of the Detroit Section, have contacted potential members and a meeting was held on the 28st of May at which time plans for organization were discussed.

Such new Sections are welcomed by the Society and the National Office will gladly be of assistance to any members who wish to take the initiative in organizing sections in other areas.

PERSONALS

W. P. RUEMMLER, formerly with The Battelle Memorial Institute in Columbus, Ohio, has recently joined The Eagle-Picher Company as a Development Engineer.

E. H. McCOY has a new position as Finishing Superintendent at the National Pressure Cooker Company in Eau Claire, Wisconsin. Mr. McCoy was formerly associated with the Chrome-Rite Company in Minneapolis, Minnesota.

JAN H. REIMERS has resigned from his position as manager of the Norwegian Industries Commission in New York, N. Y. and has become affiliated with the Aluminum Company of Canada Limited in Arvida, P. Q., Canada.

WM. W. WINSHIP, formerly manager of The Thermal Syndicate Ltd., has announced the founding on June 1st of Winship Silica Products Company in Freeport, L. I., New York.

LOOK APPLAUDS JACK DeMENT

Jack DeMent, a member of The Electrochemical Society since 1940, is honored in the May 11th issue of LOOK Magazine as one of America's leading scientists. Now only 28, he was one of the 21 U. S. scientists invited to Bikini in 1946.

Mr. DeMent published his first scientific paper at 13 and his first book came out six years later. Further, he has written or contributed to 12 books and more than 100 scientific papers on atomic energy, radioactivity, fluorescence, phosphorescence, and fluorochemistry, and has obtained or applied for more than 50 patents, 17 of which have been assigned to the Atomic Energy Commission. In addition, he is recognized as the originator of DeMent's Law of Fluorescence.

A graduate of Reed College in Portland, Oregon, Mr. DeMent is now doing Navy research work. According to LOOK, "His favorite hobby to lift this weight of brainwork off his mind: weight-lifting."

BOOK REVIEWS

PHOTOELECTRIC CELLS by A. Sommer. Published by Chemical Publishing Company, Brooklyn, N. Y. 104 pages, $2.75.

During the past decade, photocathodes of the Caesium-Antimony type have been widely used as photoelectric emitters because of their superior quantum efficiency and low dark current. Since most of the standard treatises on photoelectricity were written before these important emitters were discovered, there is a definite need for literature reviewing the recent developments in this field.

This brief monograph partially fulfills this need. It is intentionally devoted entirely to photocells of the emission type and is not concerned with barrier-layer or photo-conduction phenomena. The most valuable chapters are those describing the manufacture and properties of photocathodes and comparing the relative advantages of vacuum, gas-filled, and multiplier photocells. In these chapters the properties of the recent (Sb-Cs) and (Bi-O-Ag-Cs) photocathodes are compared with the earlier (Ag-O-Cs) emitters. The points to be considered in selecting the most suitable type for a partucular purpose are emphasized.

Because of its brevity, this monograph can give only a superficial discussion of the theory and practical applications of photoelectric emission. Hence, it does not meet the needs of the physicist who desires a discussion of photoelectric phenomena according to modern semi-conductor theory and it will not satisfy the electronics engineer interested in the details of recent military and television applications of photoelectricity. However, the reader requiring a brief, qualitative description of modern photocathodes may find this book helpful.

J. A. BURTON

THE SYSTEMATIC IDENTIFICATION OF ORGANIC COMPOUNDS by Ralph L. Shriner and Reynold C. Fuson. Published by John Wiley & Sons, Inc., New York. Third Edition, 1948. $4.00.

This book is the latest edition of a text which has enjoyed wide popularity for about fifteen years. There has been some rearrangement and revision, mainly in the interest of improved teaching value. The course has been streamlined to some extent and, when it is used as intended, the qualified student spends less time in exercises and more in the solution of actual problems, although the exercises are still present for those who need them. In addition to its excellence as a manual for teaching organic qualitative analysis, the book is packed with information on methods, and with charts and tables of chemical data which make it very useful as a reference book for research workers and industrial analysts.

B. S. BIGGS

VARNISHED CLOTHS FOR ELECTRICAL INSULATION by H. W. Chatfield and J. A. Wredden. Published by Chemical Publishing Company, Inc., Brooklyn, N. Y. $6.00.

This book brings together a great deal of useful information on the subject and should be of value to those engaged in this field. The material is of a practical nature and contains very little of fundamental character. Improvement could have been made in the organization of the text. Illustrations are useful, although the captions are often inadequate. The most unsatisfactory feature of the work is the casual way in which references are given—omission of authors' names and the volume in which the references appears.

D. B. HERRMANN

ZEITSCHRIFT F. ELEKTROCHEMIE RESUMED

The Deutsche Bunsen-gesellschaft announces that resumption of publication of the "Zeitschrift f. Elektrochemie" has been authorized by the military occupation authorities. It is planned to publish six issues of 48 pages each during the year. The first issue was published in February. It is proposed that the arrangement for exchange of subscriptions with the publications of The Electrochemical Society in effect before the War be resumed. While arrangements have not been fully concluded, it is likely that the Society will offer one subscription of the Journal for two of the Zeitschrift. This would establish a subscription rate of $5.00 a year for the German periodical. Subscription before the war was $10.00 for twelve issues. Will members of The Electrochemical Society who would like the Zeitschrift f. Elektrochemie u. Angewandte Physikalische Chemie at $5.00 a year please advise the Secretary at their earliest convenience. It is unnecessary to remit the proposed subscription price at this time; subscribers will be billed upon receipt of the periodical.

Letters to the Editor

Dear Sir:

I wish to express to you my sincere appreciation for the hospitality shown me at the recent meeting of the Society in Columbus. It was a privilege to sit at the speaker's table with men so well-known for their scientific accomplishments.

The judges have bestowed upon me a great honor in the award of the Young Author's Prize for 1948. I will do my utmost to live up to this honor.

Henry Leidheiser, Jr.
University, Virginia

Dear Sir:

May I take this opportunity to thank The Electrochemical Society and quite especially the President for the great kindness which I was shown at your Columbus Meeting.

Peter Pringsheim
Chicago, Illinois

Dear Sir:

I have read with interest the editorial "Scientists Are Born That Way," in the March issue and, in my opinion, it is essentially sound and timely. Capacity for creative work is native and relatively rare, although perhaps more prevalent than we suspect. One of the major blunders in our society is that of failure to recognize and to encourage the development of unusual capacity, while our mode of educational discipline all too generally stifles capacity for creative achievement. Mass education is not educational; assembly-line production is a travesty upon intellectuality; stereotypy is the equivalent of situations which Francis Bacon was disposed to call mental blinders. Doctoral work, with which the editorial is especially concerned, is no exception to such evils, and I am glad that the writer speaks plainly about a condition that needs to be corrected.

The editorial is aimed at one area, and I am disposed to say that it hits the bull's eye. But will you be good enough to follow with another editorial setting forth a clear exposure of educational conditions preliminary to doctoral work—conditions that often prove fatal to competent young men who desire to do a superior type of graduate work. For example, as Chairman of our Committee on Graduate Studies, as well as a teacher of undergraduates, I have discovered that students are rarely encouraged to use creative ability. They more often than not take the line of least resistance in selecting courses of study; they feel that they have done well when they have "mastered" a text-book and lecture notes sufficiently to make fair grades; they are not taught the value of ideas, except perhaps vaguely in some historical sense; they rarely discuss a subject, and less frequently write an evaluation of it. The plain fact is that the vast majority of college students can neither read nor write intelligently. Our notion of education is one of mechanics—parrots, phonograph records, wire recorders. It is tragically negligent of foundational disciplines essential to creative imagination in science and other major fields.

You will be interested in a small class which I am directing this session. I am not quite certain what the relation is to philosophy, but the class will have read at least twenty-five valuable books by the end of the session. The authors include Homer, Virgil, Aristophanes, Sophocles, Thucydides, Marcus Aurelius, Epictetus, Dante, Augustine, Machiavelli, Nietzsche, Hobbes, Bacon, Sorokin, James, Goethe, and Greene. You will immediately guess my motive.

A. C. Reid
Wake Forest, N. C.

Dear Sir:

I was most interested in Dr. Storey's article on the reviewing of papers, published in the February number of the new Journal of The Electrochemical Society.

All the six questions which the reviewer is requested to answer are very much to the point. I wonder whether you would allow me to suggest a seventh—which concerns a matter that the reviewer should be asked to state whether there is evidence that the author of the paper has made a careful study of the literature, consulting the *original papers*, including those published *right up to the time* at which the paper was written.

So often, there is evidence that an author has merely consulted abstracts, or

perhaps, some comprehensive text-book. Obviously, this is quite insufficient owing to the abbreviation which must always occur, even when the author of the text-book happens also to be the author of papers; (speaking as one who is guilty of having written both papers and text-books, I would say that the space given to any particular matter in one of my papers is contracted to less than 1/10th of its original length when the subject is introduced into the book). Apart from any question of compression, it is obvious that even a freshly published text-book will not contain the most recent experimental work.

I do not suggest for a moment that the fault indicated is confined to one journal or that it occurs only on one side of the Atlantic. A particulary bad case, which happens to be before me at the present time, refers to a British author who has sent in a paper dealing with a subject on which dozens of papers have been published in the the last year or two, but without including a single reference later than *1936* (except for references to his own work). Clearly these older references have not been consulted in their journals, but have been taken from a text-book published about 1936, since one of them is merely given as "1936 (Preprint)"; if the author had consulted the original journal, the *page* would surely have been quoted.

I would venture to suggest that a journal which commences to take a rather strict attitude in regard to this matter will gain greatly in prestige, and the investigators will *themselves* benefit, since much of the work which is being published today would have been done better had the experimenters been compelled at the outset to make a real study of what had been accomplished in other laboratories—including those in distant countries. I believe that, if The Electrochemical Society were to take the lead by insisting on a real study of the literature, other journals would follow its example, and that everyone would express gratitude to your Committee for having "broken the ice."

U. R. Evans
Cambridge, England

Dear Sir:

Please excuse me if I now ask a great favor but I have no one else there to turn to. My husband, who died in 1944, was associated with your society from 1910 to 1942. He attended the Internation Chemical Congress there in 1912 and made a trip through America. As long as it was possible he was a member of the Electrochemical Society. Since he died at the age of 82 it is probable that his American friends are not now alive and so I must make my request to you. If it is at all possible please send me a CARE package. You undoubtedly are aware how difficult living conditions are here. I am fully prepared to compensate for your expenses as soon as the possibility to do so is again at hand.

With best thanks for your friendly consideration,

Frau Else Schrey
Langenbergweg 10
Radebeul II
Germany

● We are advised that CARE packages are not accepted for Radebeul which is in the Russian zone of occupation.—Ed.

SYMPOSIUM ON ELECTRON AND LIGHT MICROSCOPY

A Symposium emphasizing the supplementary relationship between electron and light microscopy, sponsored by Armour Research Foundation of Illinois Institute of Technology and the Physics Department of the Institute, was held at The Stevens Hotel, Chicago, Illinois, June 10th, 11th, and 12th. The three-day session consisted of invited papers and planned discussion covering instrumentation, techniques, and application of both electron and light microscopy. Thursday and Friday consisted of general meetings while Saturday was devoted to panel discussions.

A number of leading microscopists in both fields presented papers on subjects which included the applications of electron and light microscopy to metals, biology, fibers, fine particles, fats and soaps, plastics, etc. In addition, there were papers covering techniques such as phase microscopy, microtomy, shadow casting and replica methods. There was ample opportunity for the interchange of ideas and problems either in large discussion groups, panel meetings, or by personal contact. In addition to these sessions there were equipment displays by well-known manufacturers of research microscopes, vacuum equipment, high speed microtomes and film materials.

A. S. T. M. TO MEET WITH THE SOCIETY

The American Society for Testing Materials Committee B-8 and its subcommittees are planning a meeting in connection with the New York City Convention of The Electrochemical Society to be held October 13–16, 1948 inclusive. The sessions of the A. S. T. M. committees will be scheduled simultaneously with several of the Society's symposia on Wednesday and Thursday, October 13th and 14th. These meetings, however, will not conflict with the symposium on electrodeposition to be held on Friday the 15th, as this discussion should be of special interest to members of A. S. T. M.

POSITIONS WANTED

METALLURGIST, B.S. (Chem.), age 36, post-graduate work in metallurgy, desires position in production and refining of non-ferrous metals. Experienced in process development applying furnace, electrolytic, and leaching methods to production and refining of copper, lead, silver, tin, cadmium, zinc, and other metals. Location secondary. Reply to Box 319, The Electrochemical Society, Inc., 235 West 102nd St., New York 25, N. Y.

CHEMICAL ENGINEER, 10 years experience in the development and operation of automatic and continuous plating equipment, desires responsible position comprising technical development of production processes, special techniques, and essential equipment. Located in Ohio, Pacific northwest preferred. Reply to Box 320, The Electrochemical Society, Inc., 235 West 102nd St., New York, N. Y.

CHEMIST-METALLURGIST, 12 years experience in electroplating, metal manufacturing, and organic finishing, desires responsible executive position with metal working concern. Reply to Box 321, The Electrochemical Society, Inc., 235 West 102nd St., New York, N. Y.

GRADUATING PH.D. in Physical Chemistry desires position in industrial research. B. A., 1942. M. S. in electroplating, 1944. Ph.D. thesis on inorganic oxidation-reduction potentials. Married Veteran. 27. Available summer of 1948. Reply to Box 322, The Electrochemical Society, Inc., 235 West 102nd St., New York, N. Y.

ELECTROCHEMIST, 32, married, Ph.D. physical chemistry specializing in electrochemistry, desires position in research and development or as assistant director of research. Five years industrial experience in electroforming, electroplating, and other phases of metal finishing. Several patent applications. Reply to Box 323, The Electrochemical Society, Inc., 235 West 102nd St., New York 25, N. Y.

POSITIONS AVAILABLE

CORROSION ENGINEER, extensive industrial experience in physical metallurgy, corrosion, and materials of construction in the chemical industry required. Location southwest. Reply to Box A-200, The Electrochemical Society, Inc., 235 West 102nd St., New York 25, N. Y.

ELECTROCHEMIST, qualified, responsible, for permanent position with established eastern dry battery manufacturer. Development and manufacturing experience in dry batteries preferred. Salary commensurate with responsibility. All replies to be held confidential. Reply to Box A-201, The Electrochemical Society, Inc., 235 West 102nd St., New York 25, N. Y.

NEW MEMBERS

At the meeting of the Board of Directors held on April 14, 1948 at the Deshler-Wallick Hotel, Columbus, Ohio, the following were elected to membership:

SVEN HELGE KNUD ATLUNG, Hellesens Enke & V. Ludvigsen 6, Aldersrogade, Copenhagen, Denmark (Theoretical Electrochem., Batteries, Dielectrics)

WM. HUGH BARKLEY, Champion Paper and Fibre Co., mailing add: Chipmunk Cottage, Albemarle Pk., Asheville, N. C. (Theoretical Electrochem., Corrosion, Alkali and Chlorine, Electrodeposition, and Power)

FREDERICK MARTIN BARRY, Scovill Mfg. Co., 99 Mill St., Waterbury 91, Conn. (Theroetical Electrochem., Corrosion, Electrodeposition)

GEORGE D. COPELAND, Foote Mineral Co., mailing add: 632 N. Easton Rd., Glenside, Pa., (Electrodeposition)

RICHARD LE ROY HARTZELL, Owens-Corning Fiberglas Corp., Newark, O. (Batteries, Electronics, Power)

ROY E. HEATH, Wyandotte Chem. Corp., Industrial Sales Div., Wyandotte, Mich. (Alkali and Chlorine and Electrodeposition)

GUSTAVE HEINEMANN, Southern Alkali Corp., mailing add: 1013 Oak Pk. Ave., Corpus Christi, Texas (Corrosion, Alkali and Chlorine)

GEORGE A. HISERT, Waterbury Companies, Inc. 835 So. Main St., Waterbury, 90, Conn. (Theoretical Electrochem., Corrosion, Organic Electrochem., and Electrodeposition)

ERIK REPSTORFF HOLTVEG, Hellesens Enke & V. Ludvigsen, Ltd., mailing add: Falkoneralle 16 III, Copenhagen, Denmark (Batteries and Electrodeposition)

SHANNON JONES, General Elec. Co., mailing add: 1829 Allendale Ave., E. Cleveland 12, Ohio (Electronics)

SAM KURLANDSKY, Burgess Battery Co., mailing add: 766 W. Lincoln, Freeport, Ill., (Batteries)

BERNARD KUSMAN, Kusman-Barzili Ltd., 79 Mercaz Mishari Ltd., Tel Aviv, Palestine (Corrosion and Electrodeposition)

WM. ALFRED LALANDE, JR., Penna. Salt Mfg. Co., mailing add: 31 Kent Rd., Upper Darby, Pa. (Alkali and Chlorine)

MARSHALL W. MEAD, Oldbury Electro-Chemical Co., Niagara Falls, N. Y. (Electrodeposition)

GORDON JOLLIFFE METCALFE, Fulmer Res. Inst., Stoke Pages, Slough Bucks, England (Theoretical Electrochem., Batteries, Corrosion, Alkali and Chlorine, Electrodeposition, Electrothermics, and Electronics)

MERNITT M. OTTO, Reilly Tar and Chemical Corp., mailing add: 5602 Winthrop Ave., Indianapolis 20, Indiana (Theoretical Electrochem. and Organic Electrochem.)

REX W. OYLER, Guide Lamp Div. G. M. C., Anderson, Indiana (Electrodeposition)

CLARENCE LANE SNYDER, National Bureau of Standards, mailing add: Walnut St., N. W., Washington 12, D. C. (Batteries)

ALBERT WOODWARD, Messers Elexcel Ltd., mailing add: 16 Wollington Grove, Liverpool, England (Theoretical Electrochem., Organic Electrochem., and Electrodeposition)

ERRATUM

In the April issue, page 55*N*, first column, line 10, the diameter of the cylindrical cell should read $1\frac{1}{8}$" instead of $\frac{7}{8}$".

AMERICAN STANDARD SPECIFICATION FOR DRY CELLS AND BATTERIES

The fifth edition of the American Standard Specification for Dry Cells and Batteries is now available as Circular C466 of the National Bureau of Standards. Advances in the dry cell industry since the last specification of this type (1941) have been incorporated in the circular. Included are new specifications for radio battery packs, a more complete standardization for hearing aid batteries, standardized socket connections for radio A, B, and C batteries, and other topics.

Circular C466 may be obtained at a cost of 10 cents from the Superintendent of Documents, Washington 25, D. C., or from the American Standards Association, 70 East 45th Street, New York, N. Y.

A set of the Transactions of The Electrochemical Society has been offered for sale. The set is in excellent condition and includes Volumes No. 18 (1910) through No. 84 (1943), No. 86, and four index volumes. Information concerning purchase of these volumes may be obtained from the office of the Secretary of the Society.

PATENTS OF INTEREST TO ELECTROCHEMISTS

Selected by Fred. W. Dodson, Chairman of the Patent Committee, from the Official Gazette

March 9, 1948

Orozco, G. H., 2,437,474, Method of Anodic Cleaning

Oxford, W. F., Jr., 2,437,475, Method of Mitigating Corrosion in Wells

Parker, H. M., 2,437,476, Differential Twin Chamber Neutron Meter

Osborg, H., 2,437,612, Process for Electrolytically Zinc Plating Magnesium and Magnesium Base Alloys

Speer, W. F., 2,437,620, Method of Coating Masses of Small Copper-Bearing Aluminum Articles

March 16, 1948

Wilson, G. P., 2,437,776, Electric Induction Furnace for Continuously Heating Metal Strip

Stareck, J. E., 2,437,865, Method of Electrodepositing Copper and Baths and Compositions Therefor

Brunner, E. M., and Mardock, E. S., 2,437,935, Radiological Measurement of the Permeability of Porous Media
Blackburn, W. E., 2,437,995, Selenium Rectifiers
Tanner, R. R., 2,438, 013, Treated Steel Sheet and Process

March 23, 1948

Morehead, C., and Gustin, D. S., 2,438,181, Fluorescent and/or Cathode Glow Lamp and Method
Alexander, F., 2,438,356, Gaseous Discharge Device

March 30, 1948

Ertzman, W. F., 2,438,550, Method of and Apparatus for Indicating the Condition of an Atmosphere
Ray, W. A., 2,428,575, Thermocouple for Pilot Burners
Taylor, A. H., 2,438,587, Phototube Containing Means to Counteract Negative Wall Charges
Williams, P. D., 2,438,732, Electron Tube Cathode
Snadecki, C. W., and Richards, W. F., 2,438,830, Radiation Pyrometer Housing for Furnaces

April 6, 1948

Bell, H. M., III, 2,438,885, Apparatus for Electroplating Rings and Discs
Brown, J. T. L., 2,438,897, Method of Plating Contact Surfaces of Magnetic Reeds
Kotterman, C. A., 2,438,923, Method and Means for Making Selenium Elements
Cunningham, G. L., and Robinson, R. S., 2,438,963, Manufacture of Alkali Metal Alcoholates
Nicoll, F. H., 2,439,181, Luminescent Screen
Schroeder, L. E., 2,439,190, Electroplating Rack
Ellingboe, E. K., 2,439,203, Process for Producing Beta-Fluoroethyl Thiolacetate
McLellan, D. S., 2,439,216, Method for Removing Metallic Iron from a Fused Alumina-Cryolite Composition
Fetterley, G. H., 2,439,290, Composition for Igniter for Rectifiers

April 13, 1948

Gresham, W. F., 2,439,425, Process for Preparing Dialkyl Esters of Dicarboxylic Acids
Good, P. F., 2,439,464, Battery Container for Airplanes
Rosenthal, F., 2,439,489, Preparation of Silver Foil
Schiffl, C., 2,439,491, Enclosed Electroplating Tank
Dinsley, A., 2,439,598, Luminescent Signalling Composition
Bramley, A., 2,439,647, Photoelectric Tube and Method of Manufacturing Same
Nordlander, B. W., 2,439,669, Chlorinated Methylpolysiloxane Resins

April 20, 1948

Atkins, C. E., 2,439,787, Ultraviolet Ray Generator
Hanley, H. R., and Jacobs, J. H., 2,439,805, Method of Electrowinning Manganese
Muddiman, E. R., and Winterhalter, W. E., 2,439,858, Conductor Roll
Campbell, J. M., 2,439,884, Method and Machine for Basing and Seasoning Fluorescent Lamps
Jones, T. R., and Bierly, N. R., 2,439,935, Indian Electroplating
Anderson, F. C., 2,440,163, Battery-Charging Apparatus and Method
Broxon, J. W., and Jesse, W. P., 2,440,167, Differential Ion Chamber

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FALL MEETING

Hotel Pennsylvania, New York, N. Y.

October 13, 14, 15, and 16, 1948

SESSIONS ON

Batteries
Electrodeposition of Metals
Electrolytic Production of Metals
General and Theoretical Electrochemistry